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ATMOSPHERIC REACTION PRODUCTS FROM HAZARDOUS AIR POLLUTANT DEGRADATION

by

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16. ABSTRACT

This research project was undertaken to investigate the products of selected hazardous air pollutants (HAPs) as they react in the atmosphere. Many hazardous or potentially hazardous organic compounds are emitted into the atmosphere and are subject to chemical change by photolysis, or by reaction with a number of highly reactive species including free radicals ozone, and nitrogen oxides. It is important to understand both the fate and the persistence of a HAP in order to assess its health significance. However, for many HAPs, the major atmospheric reaction products have not been identified. The first phase of this study entailed a literature survey to determine what reaction product information was available for an initial selection of 15 target HAPs. In the second phase of the research, a number of the target HAPs were studied in Battelle's 17.3 m^3 smog chamber to determine major reaction products and to derive an estimate of atmospheric lifetime. Those HAPs examined experimentally include propylene oxide, epichlorohydrin, toluene, acrylonitrile, trichloroethylene, benzene, p-dichlorobenzene, aniline, nitrobenzene, chlorobenzene, o-cresol, and phenol. Following the chamber studies, the third phase of the research was devoted to development of field-compatible sampling and analysis methods for those HAP reaction products which: (1) represent a potential hazard and (2) for which current methods are unavailable or unsuitable.

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ABSTRACT

This research project was undertaken by Battelle's Columbus Laboratories to investigate the products of selected hazardous air pollutants (HAPs) as they react in the atmosphere. Many hazardous or potentially hazardous organic compounds are emitted into the atmosphere and are subject to chemical change by photolysis, or by reaction with a number of highly reactive species, including free radicals, ozone, and nitrogen oxides. It is important to understand both the fate and the persistence of a HAP in order to assess its health significance. However, for many HAPs, the major atmospheric reaction products have not been identified. The first phase of this study entailed a literature survey to determine what reaction product information was available for an initial selection of 15 target HAPs. In the second phase of the research, a number of the target HAPs were studied in Battelle's 17.3 m^3 smog chamber to determine major reaction products and to derive an estimate of atmospheric lifetime. Those HAPs examined experimentally include propylene oxide, epichlorohydrin, toluene, acrylonitrile, trichloroethylene, benzene, p-dichlorobenzene, aniline, nitrobenzene, chlorobenzene, o-cresol, and phenol.

Following the chamber studies, the third phase of the research was devoted to development of field-compatible sampling and analysis methods for those HAP reaction products which:

(1) represent a potential hazard and

(2) for which current methods are unavailable or unsuitable.

This report presents the results of the literature survey, the preliminary reaction product results, and the details of the sampling and analysis methods developed for several HAP reaction products.

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SECTION 1

INTRODUCTION

Organic compounds emitted into the atmosphere are subject to chemical reactions due to the presence of a number of highly reactive species, including free radicals, ozone, nitrogen oxides and similar materials. In certain cases the reaction products of the organic compounds may be even more hazardous than the starting compounds. Sampling and analysis methods have not been tested and validated for the reaction products of most hazardous air pollutants (HAPs), and in many cases, current methods are probably not suitable for field measurements of these species. Indeed, for many HAPs of interest, the major atmospheric reaction products have not even been identified.

In order to understand the impact of chemical reaction products of HAPs, it is necessary to define the nature of the major reaction products and then assess the degree of hazard by measuring the concentrations of important products in the field. The major objectives of the study reported herein were as follows:

(1) Identification of major reaction products of certain HAPs of particular interest.

(2) Development of sampling and analysis methods for field measurement of the reaction products.

The specific HAPs deemed to be of particular interest are listed in Table 1. A three phase approach was taken to achieve the project objectives:

(1) A literature review was conducted to obtain background information pertinent to chemical reactions of each compound to predict the likely atmospheric reaction products of each compound.

TABLE 1. HAZARDOUS AIR POLLUTANTS
TARGETED FOR THIS STUDY

Acetone	Methylene Chloride
Acrylonitrile	Propylene Oxide
Benzene	Perchloroethylene
Chloroform	Toluene
1,4-Dichlorobenzene	Trichloroethylene
Epichlorohydrin	Vinylidene Chloride
Ethylene Oxide	Phenol
Ethylene Dichloride	Cresols
Dibenzofuran	Nitrobenzene
Aniline	Chlorobenzene

(2) When insufficient information was available concerning the atmospheric reaction products of a compound, laboratory experiments were conducted using a smog chamber to simulate atmospheric conditions. The major products were determined using screening techniques, including cryogenic trapping gas chromatography, HPLC, and atmospheric pressure ionization triple-stage mass spectrometry.

(3) As a final phase, methods were developed for the determination of the reaction products identified in Phases 1 and 2. Since only a limited number of methods could be developed within the project resources, emphasis was placed on those products believed to be of general concern.

The specific conclusions, experimental techniques employed and results obtained are discussed in subsequent sections of this report. The findings of the Phase 1 literature review, upon which much of the experimental approach was based, are presented in the Results and Discussion section.

SECTION II

SUMMARY AND CONCLUSIONS

This report describes an experimental program undertaken to identify atmospheric reaction products of selected hazardous air pollutants (HAPs), and to develop sampling and analysis methods for those products which may be hazardous themselves. The study was not designed to be comprehensive, but rather to provide a preliminary assessment of selected HAPs and a limited methods development effort for potentially hazardous reaction products.

A literature survey was conducted in the initial stages of the project to determine what reaction product information was available for an initial list of 15 HAPs. This initial list of target HAPs is given below.

trichloroethylene	p-dichlorobenzene
vinylidene chloride	perchloroethylene
epichlorohydrin	acetone
ethylene oxide	dibenzofuran
propylene oxide	methylene chloride
acrylonitrile	chloroform
toluene	ethylene dichloride
benzene	

The conclusion from the literature survey was that insufficient reaction product data were available for 7 of the target HAP compounds. These compounds included:

acrylonitrile	p-dichlorobenzene
epichlorohydrin	propylene oxide
benzene	toluene
trichloroethylene	

Preliminary product screening experiments were conducted in a 180 l irradiation chamber. Subsequently, more comprehensive experiments to identify reaction products were undertaken in a 17.3 m^3 smog chamber. Concentrations employed in these chamber experiments were nominally 5 ppm(v) of the target HAP

and 0.5 ppm NO_2 in a background of ultrahigh purity air. Standard measurements made during these experiments included ozone, nitric oxide, nitrogen dioxide, carbon monoxide, methane, total hydrocarbon, temperature, and relative humidity. More specialized measurements were made for the target HAP, peroxyacetyl nitrate, and organic reaction products, by gas chromatography (GC); individual aldehydes, dialdehydes, and ketones by a derivatization/HPLC analysis procedure; certain chlorinated carbonyl compounds, by an HPLC method developed during this program; and a variety of organic reaction products, by mass spectrometry/mass spectrometry (MS/MS) utilizing a Sciex, Inc. TAGA instrument which was connected to the smog chamber for a limited time.

In the later stages of the project, five compounds were added to the list of target HAPs. These compounds included aniline, nitrobenzene, chlorobenzene, o-cresol, and phenol. These species were screened for atmospheric reaction products in the 17.3 m^3 chamber, but under a different set of reaction conditions. Because these compounds were expected to be rather unreactive, they were studied in mixture with a reactive two component hydrocarbon mixture. Nominal concentrations for these experiments were 1.0 ppm of the target HAP, 1.0 ppm propylene, 3.0 ppm butane, and 0.5 ppm NO_2. The same sampling and analysis methods were employed as in the earlier experiments, with the exception that the MS/MS, which was unavailable, was replaced by a GC/MS system. A new method for determining phenolic compounds also was developed/implemented during these experiments. In addition, high volume filter samples were collected from the chamber at the end of experiments which produced significant quantities of particulate matter. In one case (aniline), the particulate sample was extracted and the extract analyzed by HPLC and GC/MS. For those experiments in which filters were collected, the filter mass loading was used to infer the fraction of reacted HAP material which was present in the condensed phase.

The results of the product screening experiments are shown in Tables 2-4. Table 2 shows the initial concentrations of the target HAP and NO_x, the irradiation time, the peak ozone concentration, and the time to maximum ozone. It is important to note that the final 5 experiments

TABLE 2. INITIAL CONCENTRATION AND MAXIMUM OZONE FROM HAP PRODUCT SCREENING EXPERIMENTS

Target HAP	Initial Target HAP Concentration, ppmC	Initial NO_x, ppm	Irradiation Time Hours	(O_3) max ppm	Time to (O_3) max, Hours
Propylene Oxide	9.15	0.469	19.5	0.188	17(b)
Epichlorohydrin	11.55	0.427	24.4	0.226	24.4(b)
Toluene	33.38	0.445	5.0	0.442	2.1
Toluene	34.45	0.448	3.1	0.404	1.9
Acrylonitrile	11.75	0.468	17.5	0.645	7.7
Trichloroethylene	8.67	0.882	6.4	1.046	5.9
Benzene	36.0	0.466(c)	22.7	0.253	10.3
p-Dichlorobenzene	32.86	0.421	24.0	0.064	20.3(b)
Aniline(a)	5.00	0.422	5.5	0.107	1.4
Nitrobenzene(a)	6.55	0.391	5.5	0.663	1.5
Chlorobenzene(a)	7.41	0.405	4.8	0.757	1.5
o-Cresol(a)	7.17	0.405	5.6	0.314	0.8
Phenol(a)	4.36	0.398	6.2	0.380	0.7

(a) Experiments carried out in the presence of 1ppmV propylene and 3ppmV butane

(b) O_3 increasing when monitoring terminated

(c) 0.23 ppm NO_2 injected after 6.8 hours

TABLE 3. TENTATIVE IDENTIFICATION OF HAP REACTION PRODUCTS FROM INITIAL SMOG CHAMBER EXPERIMENTS (METHODS NOTED)

Propylene Oxide	Epichlorohydrin	Trichloroethylene	Acrylonitrile	Toluene	Benzene	p- Dichlorobenzene
Formaldehyde[1]	Acetone (artifact?)[1,2]	Phosgene[1]	Formaldehyde[1]	Formaldehyde[1]	Peroxyacetyl nitrate[3]	Dichlorophenol[2]
Acetone (artifact?)[1,2]		Formyl chloride[1]	PAN-type compound[3]	Benzaldehyde[1,2]	Phenol[2]	Dichloronitrophenol[2]
		Dichloroacetyl chloride[1]	HO C(O) CN[2]	Glyoxal[1]	Nitrophenol[2]	
		Chloroform[3]		Methyl glyoxal[1]	Nitrobenzene[2]	
		Carbon monoxide[3]		Peroxyacetyl nitrate[3]	Glyoxal[2]	
		PAN-type compound[3]		Butenedial[2]	Butenedial[2]	
				4-Oxo-2-pentenal[2]	4-Oxo-2-butenoic acid[2]	
				2-Oxo-2-butenoic acid[2]		
				2-Oxo-2-pentenoic acid[2]		
				2-Butenal[2]		
				Nitrotoluene[3]		
				o-Cresol[3]		
				2-Butenoic acid[2]		
				Nitrocresol[2]		
				Benzylnitrate[2]		

(1) HPLC

(2) API MS/MS

(3) GC

TABLE 4. REACTION PRODUCTS TENTATIVELY IDENTIFIED IN PRODUCT SCREENING STUDIES

Aniline	Nitrobenzene	Chlorobenzene	o-Cresol	Phenol
Nitrobenzene(1)	2-Nitrophenol(2)		Nitrocresol(2) (two isomers)	4-Nitrophenol(2)
Nitrosobenzene(1)	4-Nitrophenol(2)			2-Nitrophenol(2)
Nitrophenol(1)	Phenolic Compounds(2)		2-Hydroxy benzaldehyde(1)	
Aminophenol(2)				
Nitroaniline(1,2)				
Benzidine(2)				
Phenol(1)				
Isocyanato benzene(1)				
Hydroxy benzonitrile(1)				
N-Phenyl formamide(1,2)				

(1) Tentatively identified by GC/MS
(2) Tentatively identified by HPLC

were conducted in a reactive mixture which generates over 0.7 ppm O_3 in the absence of the HAP compounds. Tables 3 and 4 show the reaction products which were tentatively identified in the screening experiments. The sampling/analysis methods providing the tentative identification are ..oted. The tentative nature of these identification is stressed. Further research is needed to confirm many of the products shown in Tables 3 and 4 and to identify additional products.

Simultaneously with the product screening experiments, a sampling and analysis methods development effort was undertaken to develop and evaluate measurement techniques for pertinent HAP reaction products.

Primary emphasis was placed on the development of an analytical method for phosgene, because 1) this compound was a reaction product of several different chlorinated hydrocarbons and 2) existing methods were not considered to be sufficiently reliable at trace (sub ppb) levels. A simple derivatization HPLC technique was developed and evaluated in detail. This method was shown to give good recovery and precision down to the 50 ppt level.

Modifications to the phosgene method were made to allow determination of formyl chloride and acylchlorides. However, further work is needed to completely validate these methods. In addition, modifications were made to NIOSH method S330 to allow determination of lower levels of phenolic compounds. This method was used to determine phenols in smog chamber studies, and may be useful for ambient analysis as well.

During these experiments, considerable experience was gained in the analysis of HAPs and HAP reaction products by atomspheric pressure ionization (API) mass spectrometry/mass spectrometry (MS/MS). This technique was especially valuable during the product screening experiments, and it represents a major advance in the state of the art for HAP monitoring. Further laboratory and field experiments are warranted to document the capabilities of this technique. The results of this study, while somewhat preliminary in nature, suggest that much important information can be learned about the fate and persistence of hazardous air pollutants through environmental chamber experiments. The knowledge gained in such studies may be used to help eliminate, or at least minimize future risks associated with exposure to airborne products of HAP reactions.

SECTION III

EXPERIMENTAL

REACTION PRODUCT SCREENING EXPERIMENTS

Two smog chamber facilities were employed for HAP reaction product screening studies. Preliminary experiments were carried out using a 180 l Pyrex chamber. The majority of the experiments made use of a 17.3 m^3 Teflon-lined chamber.

The 180 l Pyrex chamber is comprised of two bell jars, each one meter tall, fastened together with an anodized aluminum ring seal. The chamber was surrounded by a bank of fluorescent black lamps. Light intensity (k_1) was 0.40 min^{-1}, as determined by NO_2 photolysis. Ultrazero purge air was supplied by cylinders (Matheson). Between experiments the chamber was evacuated and then purged with a continuous flow of clean air overnight. Materials were injected into the chamber through ports in the aluminum ring. Liquids were injected through septa ports and gases through 1/4 in. Teflon tubing. All samples were collected through 1/4 in. Teflon tubing. The chamber is equipped with a magnetically driven, variable speed, Teflon-coated stirring fan. Instrumentation employed to monitor HAP reaction products in the 180 l chamber included a Varian 3700 capillary column (fused silica, OV-1) gas chromatograph equipped with flame ionization, electron capture, and photoionization detectors. A Varian Hi Fi III with electron capture detector was used to determine PAN and other volatile organic nitrates. Nitrogen oxides were measured with a Thermo Electron Model 14 T chemiluminescence monitor and O_3 by a REM Model 612-B chemiluminescence monitor. Carbonyls were collected in a solution of dinitrophenyl hydrazine (DNPH) in acetonitrile, and the derivatives analyzed by HPLC. Halogenated acyl chlorides were sampled in a solution of aniline in toluene and analyzed by HPLC. Details of this procedure are described

later in this section. The 180 l chamber experiments were initiated with 3.5-4.0 ppm (v/v) of the test HAP and 1.5 ppm NO_2.

The 17.3 m^3 chamber employed for the majority of the product screening studies is shown schematically in Figure 1. The chamber and its operation have been described in detail elsewhere.(1) For these experiments, chamber background air was supplied by an Aadco, Inc. ultra-clean air generator. Experiments were run at 30 $\pm$ 2 C at a relative humidity of 10 percent. Light intensity (k_1) as determined by NO_2 photolysis in clean air was 0.22 min^{-1}. The chamber dilution rate, which includes air withdrawn for sampling requirements, was 0.052 hr^{-1}. Experiments with propylene oxide, epichlorohydrin, toluene, acrylonitrile, benzene, p-dichlorobenzene, and trichloroethylene employed initial concentrations of 5 ppm (v/v) of the organic compound and 0.5 ppm NO_2. Experiments with aniline, nitrobenzene, chlorobenzene, o-cresol and phenol employed 1 ppm (v/v) of the test HAP in a mixture with 1 ppm (v/v) propylene, 3 ppm (v/v) butane and 0.4 ppm NO_2. These compounds were studied in the propylene/butane matrix because their reactivity was expected to be too low to obtain measurable conversion to products if they were irradiated alone. Baseline experiments were run with the propylene/butane/NO_2 mixture alone, in order to develop a baseline against which the experiments with the test HAPs could be compared.

The analytical instrumentation and procedures employed to monitor the reactions in the 17.3 m^3 chamber are listed in Table 5. The methods employed for oxygenated halocarbons (phosgene, formyl chloride, etc.) and phenolic compounds were developed/modified as part of this Work Assignment and are described later in this section. The GC, GC/MS, MS/MS and DNPH techniques are described below. A Hewlett-Packard Model 5880 gas chromatograph with microprocessor control and integration capabilities was used to determine C_4 to C_{12} hydrocarbons. The sampling procedure involved passing a specific volume of air (up to 500 cc) through a freeze-out sample trap (15 cm long by 0.2 cm I.D. stainless steel tubing) filled with 60/80 mesh silanized glass beads. Sampling was initiated by immersing the trap in a Dewar of liquid argon (-186°C). Injections were accomplished

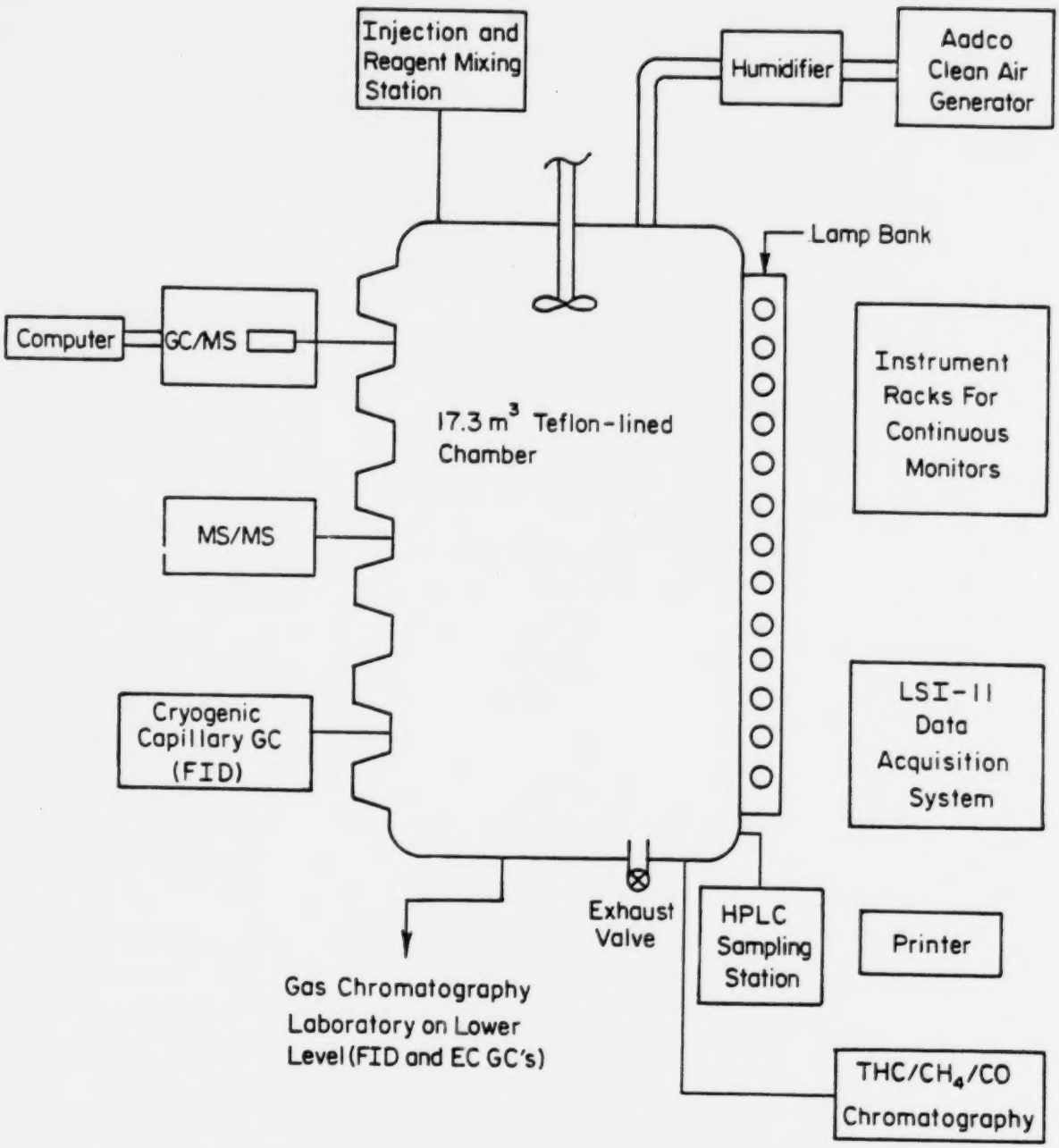

Figure 1. Schematic of 17.3 m^3 Smog Chamber.

TABLE 5. METHODS EMPLOYED FOR MEASUREMENTS IN THE 17.3 m^3 CHAMBER

Variable	Method	Instrument
Temperature	Thermocouple	EG&G 911
Dew Point Temperature	Condensation/transmission	EG&G 911
Relative Humidity	Condensation/transmission	EG&G 911
UV Intensity	Photometric	Eppley Radiometer
C_4-C_{12} Hydrocarbons	FID/GC	Hewlett Packard 5880
Organic Species	GC/MS	Hewlett Packard 5710/Extranuclear Labs SpectrEL
Organic Species	MS/MS	Sciex TAGA
Oxygenated Organics	DNPH/HPLC	Varian Model 5000
PAN, Organic Nitrates	EC/GC	Varian 3700
Phenolic Compounds	NaOH Collection/HPLC	Varian Model 5000
Oxygenated Halocarbons	Collection in Aniline/HPLC	Varian Model 5000
CH_4/CO	FID/GC	Beckman 6000
Total Hydrocarbons	Heated Probe FID	Beckman 402
Ozone	UV Photometry	Dasibi 1003 AAS
Nitrogen Oxides	Chemiluminescence	Monitor Labs 8440

by transferring the collected sample from the trap through a heated (150°C) six-port valve (Carle Instruments Model 5621) and onto the analytical column. The components in the trap were flash evaporated into the gas chromatograph by rapidly heating a thermocouple wire which was wound around the sampling trap. During normal operations the trap was heated from liquid argon temperature to 150°C within 20 seconds. The sample line was maintained at 150°C.

A 50-meter OV-1 wide-bore fused silica column (Hewlett Packard) was used to separate the C_4 through C_{12} organics. Optimum results in component resolution were achieved by temperature programming from -50 to 150°C at 8 degrees/minute.

Calibration of the gas chromatographic system was accomplished by injecting an external standard mixture into the GC. A ppbC response was determined and the value obtained was then assigned to all identified and unidentified compounds (i.e., 1 ppbC propane responds the same as 1 ppbC hexane, etc.). The standard mixtures were calibrated against several NBS propane and benzene primary standards.

A Sciex, Inc. Trace Atmospheric Gas Analyzer (TAGA 6000) was utilized for product screening experiments with propylene oxide, epichlorohydrin, acrylonitrile, trichloroethylene, benzene, toluene, and dichlorobenzene. The instrument was only available for a limited time. Later experiments for which the TAGA was unavailable made use of a GC/MS system coupled directly to the smog chamber. The TAGA is an atmospheric pressure ionization (API) quadrupole mass spectrometer with MS/MS capability. For these experiments the TAGA was connected directly to the smog chamber through 1/4 in. diameter Teflon tubing and a 1/2 in. diameter quartz inlet tube. The instrument was operated at a sampling rate of 20 liters min^{-1}. Continuous sampling at this rate would cause excessive dilution of the chamber contents, so the instrument was only connected to the chamber for 10 minutes out of each hour. At the conclusion of each experiment, potential reaction product peaks (i.e. peaks which grew during the irradiation) were analyzed in the MS/MS mode. The first quadrupole was tuned to pass the particular mass of interest into an intermediate chamber

where the molecular ion was fragmented by collisionally induced decomposition (CID) with argon atoms. The fragment ions were then analyzed by the final quadrupole.

For the later experiments, for which the TAGA was unavailable, we utilized a dedicated, highly sophisticated quadrupole mass spectrometer which was interfaced to a Hewlett Packard 5710 GC. The Extranuclear Laboratories SpectrE1 instrument has a range up to 1200 amu and is equipped with an array of computerized data handling, printing and plotting services with software tailored to the research needs of the smog chamber facility. Four sample ionization modes are possible with the mass spectrometer; conventional electron impact (EI) ionization, chemical ionization (CI), dual simultaneous EI/CI, and atmospheric pressure ionization (API). The instrument can be tuned to operate in either a positive ion or negative ion mode. For the experiments reported here, the mass spectrometer was operated in the EI mode.

The data system for the gas chromatograph/mass spectrometer has been designed around a Digital Equipment Corporation (DEC) PDP 11/23 central processor with dual RLO2 disk drives. Interfacing in real time is accomplished by use of A/D converters, parallel and serial interfaces, 12- and 16-bit DAC boards and a 1 Mhz real-time clock. Data was acquired in analog mode via the A/D converters.

Carbonyl compounds were collected in liquid impingers containing 2,4-dinitrophenylhydrazine (DNPH) wherein the DNPH derivatives were formed. The derivatives were extracted into an organic solvent, concentrated, and analyzed by high performance liquid chromatography (HPLC) using a UV detector.

The procedure utilized an impinger solution consisting of 250 mg of 2,4-dinitrophenylhydrazine and 0.2 ml of 98 percent sulfuric acid dissolved in 1 liter of acetonitrile (ACN). This reagent was prepared within 72 hours of sampling. A 10 ml volume of the ACN/DNPH reagent was used. Samples were collected from the smog chamber at 1 liter/minute for 20 minutes. The impinger contents were transferred to a 10 ml graduated cylinder and the impinger rinsed with 1-2 ml of ACN, which was then delivered

into the graduated cylinder. The final volume was adjusted to 10 ml with ACN and the sample was placed in a 20-ml glass vial having a Teflon-lined screw cap. The vial was labeled, sealed with Teflon tape, and placed in a charcoal-containing metal can until analyzed.

The ACN/DNPH samples were analyzed by HPLC with UV detection at 370 nm. The amount of each aldehyde was determined from response factors for pure DNPH derivatives. A Zorbax ODS (4.6 x 25 cm) column and 80/20 methanol/water mobile phase were used for the HPLC separation. The instrument was calibrated daily by injecting a standard containing 2 mg/l of each DNPH derivative of interest. In addition, the chamber DNPH samples were analyzed for dicarbonyl compounds (glyoxal, biacetyl, and methyl glyoxal) by a modified procedure. This procedure involved heating the sealed vial at 65-70°C for one hour using an aluminum heating block, evaporating the sample to dryness using a stream of high purity nitrogen gas at 65-70°C, and dissolving the residue in 2 ml of acetonitrile. This solution was analyzed for glyoxal, methyl glyoxal, and biacetyl using the same HPLC conditions as described above except that a UV detector operating at 254 nm and a 75/25 ACN/water mobile phase was employed.

At the conclusion of three experiments which generated substantial amounts of aerosol (i.e. aniline, o-cresol, and phenol), the chamber contents were sampled through a high purity quartz fiber filter (Pallflex QAST). The filter from the aniline experiment was cut in half and one half was extracted overnight (Soxhlet) in methylene chloride. The extract was concentrated to 300 ul and analyzed by GC/MS. The remainder of the extract was exchanged into acetonitrile and diluted to 3 ml for HPLC analysis. The conditions employed for HPLC analysis were:

Column -- Lichrosorb RP-2, 5 um, 25 cm by 4.6 mm

Mobile Phase -- 50/50 acetonitrile/pH 4.5 acetate buffer

Injection Volume -- 20 ul

Flow Rate -- 1 ml min^{-1}

Detector -- electrochemical at 0.6 volts.

The other half of the filter from the aniline experiment and the filters from the o-cresol and phenol experiments were sealed in glass petri dishes, further sealed in Tedlar bags, and stored at -20°C for possible future analysis.

SAMPLING/ANALYSIS METHODS FOR HAP REACTION PRODUCTS

HPLC Procedure for the Determination of Phosgene

The concept chosen for evaluation and optimization in the determination of phosgene involved the reaction of phosgene with aniline to form carbanilide (N,N'-diphenylurea) in an impinger, and subsequent determination of this compound by HPLC with a UV detector. Toluene was selected as the impinger solvent due to its relatively high boiling point and inert nature. Experiments were conducted to optimize the aniline concentration, sample flow rate and time, sample preparation procedure, and HPLC conditions.

All HPLC work was conducted using a Varian Model 5000 gradient system equipped with a Laboratory Data Control Model 1203 fixed wavelength (254 nm) UV detector. A Zorbax ODS (25 cm x 4.6 mm ID) column was employed throughout the study. Optimal HPLC separation conditions were achieved using a 50/50 acetonitrile/water mobile phase at a flow rate of 1 ml/minute. Under these conditions carbanilide eluted at approximately 7 minutes.

The sampling and analysis scheme selected based on the results of various laboratory experiments is as follows. A 10-100 liter volume of air was sampled through a midget (jet-inlet type) impinger containing 10 ml of a 2 percent (by volume) aniline in toluene solution. The sampling rate did not exceed one liter/minute. The impinger contents were placed in a 20 ml vial fitted with a Teflon-lined screw cap, the impinger was rinsed with 5 ml of toluene, the rinse solvent was added to the vial, and the vial was transported to the laboratory for further processing. In the laboratory the sample was taken just to dryness by heating to 50°C on an aluminum heating block under a gentle stream of clean nitrogen

gas. The residue was immediately dissolved in 0.5 ml of HPLC mobile phase and stored refrigerated until analyzed. Generally a 60 ul portion of the sample was injected onto the HPLC system.

Two systems were used to generate gas phase standards of phosgene down to the sub-ppb level. The first system, shown in Figure 2, was a dynamic dilution system using a phosgene permeation tube (from Analytical Instrument Development Corp.) which released approximately 800 nanograms per minute of phosgene at 30°C. When desired the dilution air was directed through a water impinger prior to contacting the permeation air stream to achieve relative humidities as high as 70 percent. At a total flow of three liters per minute this system was capable of delivering a phosgene concentration of approximately 3 ppb with the permeation tube thermostated at 15°C. To obtain even lower phosgene concentrations the permeation system was connected to the 17 cubic meter Teflon-lined smog chamber, described in the previous section, for the desired period of time. Phosgene concentrations as low as 200 ppt were achieved in this manner, and such standards appeared to be stable for at least several hours.

HPLC Determination of Formyl Chloride

Formyl chloride reacts with aniline in an analogous fashion to phosgene, to yield formanilide. Since this compound can be readily determined by HPLC some effort was directed towards developing a parallel procedure to the phosgene procedure described above. However, formyl chloride is quite unstable at room temperature, decomposing to CO and HCl, and consequently all work was conducted using formanilide as the test compound in order to evaluate the method recovery and precision (i.e. the derivatization step itself could not be directly evaluated).

The greater volatility and water solubility of formanilide, relative to carbanilide, created the need for modifications in both the sample preparation and HPLC analysis steps of the procedure previously described for phosgene determination. The impinger solution was evaporated to 1 ml, rather than to dryness, to avoid volatilization of formanilide. The concentrated solution was then diluted to 10 ml with hexane and was shaken

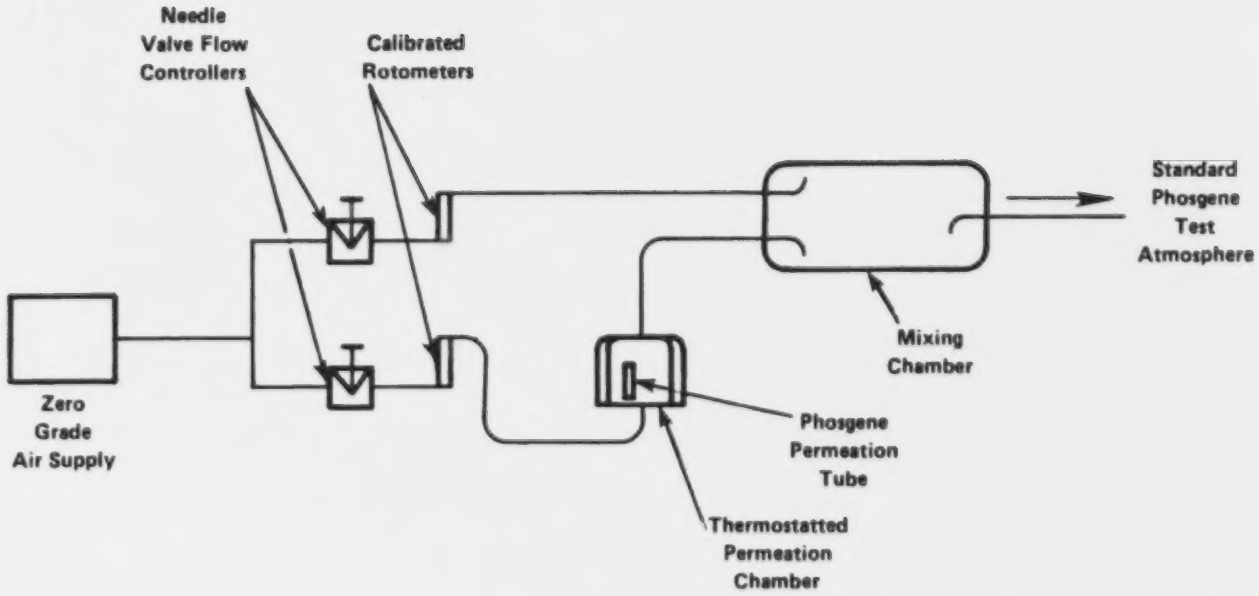

Figure 2. Schematic Diagram of Apparatus for Generating Phosgene Test Atmosphere.

with 1 ml of water in a 15 ml glass stoppered conical centrifuge tube. The water layer was analyzed for formanilide, using the HPLC conditions described earlier for phosgene except that a 20/80 acetonitrile/water mobile phase was employed. Under these conditions the retention time for formanilide was approximately 12 minutes.

Determination of Acyl chlorides by GC/ECD

Acyl chlorides react with aniline to form the corresponding anilides. Consequently some attempts were made to use the phosgene procedure described above for the determination of mono-, di-, and trichloroacetylchlorides, which are known reaction products of several HAPs. However, initial results showed GC/ECD to be superior to HPLC in terms of sensitivity and specificity. The good sensitivity of GC/ECD allowed direct injection of the aniline/toluene impinger solution, without preconcentration, to be a viable approach. In fact, preconcentration of the sample was found to be detrimental to the GC performance because of the large amount of aniline injected onto the column.

Optimal GC operating conditions were found to be as follows:

Column - DB-5, fused silica, 50 meter x 0.25 mm ID, J & W Scientific

Linear flow rate - 30 cm/sec, nitrogen

Temperature program - 80° - 200°C at 20°C/minute

Injection - 2 ul splitless

Injector temperature - 250°C

Detector temperature - 300°C

Attempts to generate stable gas phase standards of the acylchlorides were not successful, due to the rapid loss of the compounds, presumably through chemical reactions. Consequently the methods were validated using hexane solutions of the compounds spiked either directly into the impinger or into the inlet arm of the impinger prior to drawing clean air through the sampling system. The three acyl chlorides were purchased

in the purest form available from Aldrich Chemical Company and were stored refrigerated in a desiccator when not in use.

Determination of Phenolic Compounds

During certain product screening smog chamber experiments, an HPLC method was implemented to determine phenolic compounds. The method is a modification of NIOSH Method 5330 for phenol in air. A 60 l chamber air sample was collected in 0.1 N NaOH in an impinger at a flow rate of 2 l min^{-1}. The samples were acidified with H_2SO_4 and analyzed by HPLC using the following conditions:

Column -- Zorbax ODS, 5 um, 25 cm x 4.6 mm

Mobile Phase -- 30% acetonitrile, 69% H_2O, 1% acetic acid

Flow Rate -- 1 ml min^{-1}

Detector -- UV at 254 nm

Injection Volume -- 20 ul.

A number of standards were run to obtain retention times and response factors. Table 6 lists the retention times of a number of phenolic compounds run under the conditions noted above.

TABLE 6. RETENTION TIMES OF PHENOLIC COMPOUNDS UNDER HPLC ANALYSIS CONDITIONS IN TEXT

Compound	Retention Time, Min.
Phenol	8.24
4-Nitrophenol	11.58
2-Methylphenol	15.12
2-Nitrophenol	22.00
2-Chlorophenol	16.62
4-Methyl-3-Nitrophenol	19.07
3-Methyl-2-Nitrophenol	16.62
5-Methyl-2-Nitrophenol	44.00
2-Methyl-3-Nitrophenol	20.00

SECTION IV

RESULTS AND DISCUSSION

The driving force behind this program is the need for sampling and analysis methods for photochemical reaction products of hazardous air pollutants. Before methods could be developed, however, it was first necessary to identify the pertinent HAP reaction products. A literature survey was undertaken in the initial stages of the program to identify the target compounds which had been studied previously for reaction products. Those for which product data was unavailable or incomplete would require further experimental work. The results of the literature survey were used to direct the subsequent tasks on product screening and methods development.

LITERATURE SURVEY OF TARGET HAP REACTION PRODUCTS

The literature survey was initiated at the start of the study to uncover previous work on atmospheric reaction products and analytical methods for the target hazardous air pollutants. The Chemical Abstracts and National Technical Information Service literature was searched by computer. Other sources of information were searched manually. Pertinent publications and reports were obtained and reviewed.

Table 7 summarizes the results of the literature survey for the target HAP compounds. A discussion of the individual compounds follows.

Trichloroethylene, $CHClCCl_3$

The photochemical behaviour of trichloroethylene in the presence of nitrogen oxides has been the subject of several studies (Appleby, A. et al. (1976), Cupitt, L. T. (1980), Dahlberg, J. A. (1969), Dilling, W. L. et al. (1976), Gay, B. W. et al. (1976)). Dichloroacetyl chloride and

TABLE 7. SUMMARY OF LITERATURE SURVEY FOR 15 HAZARDOUS AIR POLLUTANTS

Compound	Estimated Atmospheric Residence Time, Days	Conditions (Reference)	Organic Products: major / minor (anticipated)
Trichloroethylene	5.2	$NO_2/h\nu$ (8)(6)(4)(5) $NO_2/H_2O/HC/h\nu$ (2)	$Cl_2HCCOCl$, HCO_2H, $COCl_2$ $CHCl_3$
Vinylidene Chloride	2.9	(6)(4)	(H_2CO), (Cl_2CO) (HCO_2H)
Epichlorohydrin	5.8	(4)	(H_2CO)
Ethylene Oxide	5.8	$NO_x/h\nu$ (13) $NO_2/h\nu$ (12)	CH_3OH, $C_2H_5ONO_2$, CH_3NO_2, CH_3ONO_2
Propylene Oxide	8.9	(4)(9)	(H_2CO) ($CH_3C(O)CHO$)
Acrylonitrile	5.6	(4)	(H_2CO) (HCO_2H) (HC(O)CN)
Toluene	1.9	$NO_x/h\nu$ (11)(1)(10)(22) (17)(24) $NO_x/C_6H_5CHO/h\nu$ (3)	H_2CO, C_6H_5CHO, o-cresol, m-cresol, Benzylnitrate, nitrocresols p-cresol, nitrotoluene, PAN, methylnitrate CH_3COCHO
Benzene		$NO_2/h\nu$ (16)(15)(10)	$C_6H_5NO_2$, $C_6H_4(OH)NO_2$, $C_6H_3(OH)(NO_2)_2$ Glyoxal, Methylglyoxal biacetyl C_6H_5OH, $C_6H_5NO_2$
p-Dichlorobenzene	39	(18) $NO_x/h\nu$ (4)(14)	2,5 Dichloro 6-nitrophenol 2,5 Dichloronitrobenzene, 2, 5-Dichlorophenol, 2,5 Dichloro 4-nitrophenol (ring cleavage products)
Perchloroethylene	67	$NO_2/h\nu$ (8)(19) (6)(4)	HCO_2H, Cl_3CCOCl CCl_4, $COCl_2$
Acetone	--	(6)(25)(26) (24) $CH_3COC_2H_5/OH$	PAN, CH_3ONO_2
Dibenzofuran	--	--	--
Methylene Chloride	83	(6)(23)(4)	($COCl_2$) (ClHCO)
Chloroform	120	$NO_2/C_2H_2/CHCl_3/h\nu$ (7)	$COCl_2$
Ethylene Dichloride	53	$Cl_2/h\nu$ (2) (4)	HCClO, $H_2CClCOCl$ $H_2CClCOCl$, H_2CO, $H_2CClCHO$

chloroform have been observed as the primary reaction products with formic acid and phosgene appearing in lower yield.

Vinylidene Chloride, CH_2CCl_2

No information has been found on the photooxidation products of vinylidene chloride. Environmental chamber studies have, however, shown it to be among the more reactive volatile chlorohydrocarbons in the presence of NO (Dilling, W. L. et al. (1976)). Anticipated photooxidation products include formaldehyde, formic acid and phosgene.

Epichlorohydrin

The photooxidation products of epichlorohydrin have not been identified. Chamber studies have, however, demonstrated good stability when irradiated in the presence of NO (Dilling, W. L. et al. (1976)). Cupitt (1980) has listed formaldehyde and other carbonyl compounds as the anticipated product of photooxidation.

Ethylene Oxide, $(CH_2)_2O$

Chamber studies have demonstrated the low photochemical activity of ethylene oxide in the presence of nitrogen oxides (Joshi, S. B. et al. (1982) Jaffe, S.). Methanol, nitromethane, methyl nitrate and ethyl nitrate have been identified by Jaffe as the organic photooxidation products.

Propylene Oxide, CH_3CHOCH_2

The photooxidation of propylene oxide does not appear to have been studied. Formaldehyde and methylglyoxal have been listed as the anticipated organic photooxidation products (Cupitt, L. T. (1980)).

Acrylonitrile, CH_2CHCN

No information has been found on the photochemical reaction products of acrylonitrile. Cupitt (1980) suggests a residence time similar to that of epichlorohydrin. Anticipated photooxidation products include formaldehyde, formic acid, and HC(O)CN. His estimated rate

constants for acrylonitrile reaction with OH and O_3 are within a factor of two of the recent measurements of Pitts et al. (1981).

Toluene, $C_6H_5CH_3$

The gas phase photochemistry of toluene in the presence of NO_x has received considerable attention because of its relevance to urban air chemistry (Akimoto, H. et al. (1978), Atkinson, R. et al. (1980), Moshito, M. et al. (1978), Hull, L. A. (1980), Nojima, K. and Hanno, S. (1977), Spicer, C. W. and Jones, P. W. (1977), Cox, R. A. et al. (1980)). Among the materials identified as primary products are benzaldehyde, nitrotoluene and o-cresol. Minor products include m and p-cresol, benzyl nitrate, nitrocresols and the ring cleavage products methyl nitrate, methyl glyoxal, PAN and formaldehyde. The ubiquitous character of atmospheric aromatic hydrocarbons suggests that their photooxidation products should be of concern. Indeed nitrocresols have been identified in precipitation in Japan (Nojima, K. et al. (1975)).

Benzene, C_6H_6

The photooxidation of benzene by OH in the presence of NO_x has been studied in chamber experiments (Hoshino, M. et al. (1978)). Nitrobenzene and phenol were observed as the major products. Nitrophenol was observed as a minor product as well. The ratio of nitrobenzene to phenol increased as the initial NO_2 concentration increased. Another report, Nojima, K. et al. (1975) cites nitrophenol derivatives as photooxidation products of aromatic hydrocarbons such as benzene and toluene in the presence of NO.

p-Dichlorobenzene, $C_6H_4Cl_2$

Irradiation of p-dichlorobenzene in the presence of NO_x produced 2,5-dichloro-6-nitrophenol as the main product (Nojima, K. and Kanno, S. (1980)). 2,5-Dichloronitrobenzene, 2,5-dichlorophenol, and 2,5-dichloro 4-nitrophenol were observed as minor products. Results were also cited

for irradiation in nitrogen and NO_x free air as well as the dark reaction with NO_x in air.

Perchloroethylene, CCl_2CCl_2

The photochemical activity of perchloroethylene has been addressed by several authors (Dilling, W. L. et al. (1976), Gay, B. W. et al. (1976), Singh, H. B. et al. (1975)). It is the least reactive of the chlorinated ethylenes in the presence of NO_2. Photodecomposition products include CCl_4 and $COCl_2$. Chlorinated acetyl chloride (primarily Cl_3CCOCl) has also been identified as a product (Gay, B. W. (1976)). Perchloroethylene reactivity has recently been reviewed by Dimitriades et al. (1983).

Acetone, CH_3COCH_3

The ozone forming potential of acetone in the presence of NO_x has been found to be very low (Sickles, II, J. E. et al. (1980)). Among the 17 compounds studied (olefins, aromatics, ketones and paraffins) acetone was the least reactive with OH. No products were identified although they may be assumed to include PAN and methylnitrate, photooxidation products of other simple ketones (Cox, R. A. et al. (1980)).

Dibenzofuran $(C_6H_5)_2O$

No information has been found on the atmospheric chemistry of dibenzofuran.

Methylene Chloride, CH_2Cl_2

Methylene chloride reacts less than five percent in 21 hours in simulated atmospheres (Dilling, W. L. et al. (1976)). Anticipated products include $COCl_2$ and ClHCO (Cupitt, L. T. (1980)).

Chloroform, $CHCl_3$

In simulated atmospheres containing chloroform (8.17 ppm), ethylene (2.2 ppm) and NO_2 (1.23 ppm) only four percent of the chloroform was consumed in 3.5 hours. Phosgene was the sole organic product identified (Gay, B. W. et al. (1976a)).

Ethylene Dichloride, CH_2ClCH_2Cl

The photooxidation of ethylene dichloride with Cl atoms has been studied in dry air containing ~0.1 ppm hydrocarbon. Ethylene dichloride was 40 percent consumed after four minutes yielding formyl chloride as the primary organic product. Chloroacetyl chloride was also observed at low yield (Spence, J. W. and Hanst, P. L. (1978)).

PRODUCT SCREENING EXPERIMENTS

It was determined from the literature survey that insufficient reaction product data were available for several of the target HAP compounds, and that experimental product screening studies were required. Eight of the original 15 target HAPs were found to require further product screening studies. In addition, five new target HAPs were added to the study after the literature survey was completed. The 12 potentially hazardous air pollutants which were subjected to product screening experiments are tabulated below:

propylene oxide	p-dichlorobenzene
epichlorohydrin	aniline
trichloroethylene	nitrobenzene
acrylonitrile	chlorobenzene
toluene	phenol
benzene	o-cresol

Experiments to identify reaction products of these potentially hazardous air pollutants were conducted in a 180 l Pyrex chamber and a 17.3 m^3 Teflon-lined environmental chamber. The experimental procedures and analytical methods employed in the product screening studies were described in Section III.

Preliminary experiments were performed to evaluate reaction rates and products of four HAPs (trichloroethylene, epichlorohydrin, propylene oxide, and acrylonitrile). The compounds were tested (individually) by placing approximately 4 ppm of the compound and 1 ppm of NO_2 in a 180 liter smog chamber and irradiating with fluorescent lamps. Periodic samples were taken for the analysis of: (1) PAN and related compounds

by GC; (2) volatile organics by GC with tandem photoionization (PID), electron capture (ECD), and flame ionization (FID) detectors; (3) phosgene, formyl chloride, and chloroacetylchlorides; and (4) aldehydes.

Epichlorohydrin reacted at a rate of approximately 0.036 hr^{-1}. No formation of formyl chloride or aldehydes was observed (formation of such products had been speculated). A small amount (approximately 10-20 ppb) of PAN or a related (possibly chlorinated) compound was observed after overnight (21 hours) irradiation. No other products were observed in this preliminary experiment.

Acrylonitrile also reacted slowly (~0.034 hr^{-1}). Aldehydes were not found (as previously speculated). Two small peaks eluting closely to PAN were observed after ~20 hours irradiation and presumably represent similar compounds (one compound possibly being PAN). Several unidentified products were apparent in the GC/PID chromatogram.

Propylene oxide also reacted at a rate of ~0.036 hr^{-1}. After overnight exposure (21 hours) several carbonyl compounds were observed as products (formaldehyde ~100 ppb, acetaldehyde ~25 ppb, propionaldehyde ~150 ppb, and a compound which might be acetone ~200 ppb). Methyl glyoxol was not detected. A small amount (~50 ppb) of PAN (or a similar compound) was also formed. Several compounds eluting after propylene oxide were detected on the GC/PID system.

Trichloroethylene reacted much more rapidly than the other compounds (~0.12 hr^{-1}) and yielded phosgene, dichloroacetylchloride, CO, chloroform, and a PAN type compound (presumably chlorinated PAN).

These preliminary experiments demonstrated a need for a wider variety of analytical methods and larger sample volumes than can be accommodated with the 180 l chamber. As a consequence, the more detailed screening experiments were carried out in the 17.3 m^3 chamber described in Section III.

Propylene Oxide

A mixture of 5 ppm (v/v) of propylene oxide and 0.5 ppm NO_2 in clean air was irradiated for 19 hours in the 17.3 m^3 smog chamber. Judging

from the total hydrocarbon data, propylene oxide reacts only very slowly, if at all, under these conditions. The organic disappearance rate was indistinguishable from the chamber dilution rate. The low level of NO present after irradiation was initiated was oxidized to NO_2 only very slowly. Ozone reached a maximum value of 188 ppb after 17 hours. After 19 hours of irradiation, formaldehyde exceeded the t = o value by 23 ppb and acetone was present at 37 ppb above the chamber background. It should be noted however, that acetone is ubiquitous in the laboratory, so that the increase noted here could be artificial. There was slight evidence from the MS/MS results for methylglyoxal production, but methylglyoxal was not observed in the DNPH/HPLC data (detection limit of 25 ppb).

In summary, propylene oxide was studied in both a 180 l and 17.3 chamber. Under conditions conducive to photochemical reactions, propylene oxide reacted only slowly, if at all. No unexpected reaction products which would require further analytical methods development were observed.

Trichloroethylene

Trichloroethylene was irradiated in the 17.3 m^3 chamber for eight hours. Starting concentrations were 5 ppm (v/v) trichloroethylene and 1 ppm NO_2. Trichloroethylene was appreciably more reactive than propylene oxide, epichlorohydrin or acrylonitrile. GC measurements yielded a trichloroethylene consumption rate of 0.128 hr^{-1}, exclusive of dilution. This is in excellent agreement with the consumption rate of 0.12 hr^{-1} determined from preliminary experiments in the 180 liter glass chamber. The maximum O_3 produced in the experiment was 919 ppb. Reports in the literature indicate that dichloroacetyl chloride, chloroform, formic acid and phosgene are reaction products. The more recent report by Edney et al.(29) reported formyl chloride and CO as products. Both CO and HCl are expected secondary products due to formyl chloride decomposition.

In the present experiments with trichloroethylene, the following products were observed: dichloroacetyl chloride, phosgene, formyl chloride, chloroform, carbon monoxide, and PAN or a PAN homolog. Chloroform was not quantified in this experiment. After five hours of

reaction, the products other than chloroform accounted for about 40 percent of the reacted trichloroethylene. API mass spectra of the chamber air before irradiation and after three hours of reaction showed increases at m/z 59, 77, 87, 91, and 101. All of these peak increases were marginal, and the mass spectra were of insufficient quality for identification of the species responsible for these signals.

This product screening experiment for trichloroethylene has confirmed the reaction products reported in several earlier studies. No previously unidentified products were revealed in this study. After five hours of irradiation, about 40 percent of the reacted trichloroethylene was accounted for as dichloroacetyl chloride, phosgene, formyl chloride and carbon monoxide. Chloroform was also observed but not quantified. The rest of the reacted trichloroethylene which was not accounted for may have been lost to the chamber walls as dichloroacetyl chloride, phosgene, or formyl chloride. It is also possible that compounds, such as acid chlorides, are formed but are not detected by the techniques employed in this experiment.

Acrylonitrile

Acrylonitrile was irradiated for 17 hours in the presence of NO_x. The initial organic/NO_x ratio was 10.0. The reactivity of acrylonitrile appeared to be somewhat greater than either propylene oxide or epichlorohydrin. The concentration of O_3 reached a maximum of 645 ppb in 7.5 hours. Judging from the total FID response, acrylonitrile was consumed at a rate of approximately 0.01 hr^{-1}, exclusive of dilution. Specific GC measurement of acrylonitrile in preliminary experiments in a 180 l glass chamber yielded an acrylonitrile consumption rate of 0.034 hr^{-1}.

No dialdehydes were observed in the DNPH/HPLC chromatogram of acrylonitrile reaction products. After 16 hours of reaction, formaldehyde was present at a concentration of 286 ppb. A compound was observed to elute from the gas chromatograph at the same retention time as PAN. If the compound is PAN, its maximum concentration is only 23 ppb. It is possible that this chromatographic peak represents a PAN homolog formed in the reaction of acrylonitrile: however, it is more

likely that PAN was actually produced during the experiment, either from organic impurities in the acrylonitrile or contaminants in the ultra-clean background air. Precautions were taken to minimize both of these sources of contamination, but it is not possible to eliminate all sources of trace organics over a 17 hour experiment, and it is likely that the apparent PAN formation is artificial. In any case, the concentration was quite low and the compound is unlikely to be a major product.

Several peaks in the atmospheric pressure ionization (API) mass spectrum of this experiment increased during irradiation. API mass spectra of the chamber air were taken before irradiation and after 16 hours of irradiation. These spectra are shown in Figure 3 A and B respectively. Note the scale change of the ordinate. The ordinate represents relative peak intensity while the abscissa displays mass. It must be noted that molecular ions generally appear at the M+1 location in API mass spectra. It should also be emphasized that clusters of H_2O molecules appear every 18 amu starting at 19. Therefore, peaks at 19, 37, 55, and 73 are generally attributable to the M+1 response of $(H_2O)_n$. The acrylonitrile peak at m/z 54 is merged with the water cluster at 55 amu in Figure 3 A. There is also some indication in Figure 3A of acrylonitrile dimer at m/z 107. Figure 3B shows evidence of small peak height increases at 43, 57, 59, 87, and 101 amu. Spectra recorded at higher resolution also showed an increase in the 72 amu peak. Fragmentation patterns of the ions at several of these masses were obtained by collisionally induced dissociation (CID) of the molecular ions in the MS/MS mode of operation. There was no library of CID spectra available for matching purposes, so tentative identification of products is based on manual review of the fragmentation patterns.

Figure 4 shows the CID spectrum of the ion appearing at m/z 72. Higher resolution was used to separate the peaks at 72 and 73. One compound which might fragment in the manner shown in Figure 4 is HOC(O)CN. However, with the available data, this identification is only speculative. The identities of the other peaks which increased during the experiment are uncertain. However, the spectra for the peaks at m/z 87 and 101 are very similar to spectra recorded for toluene reaction

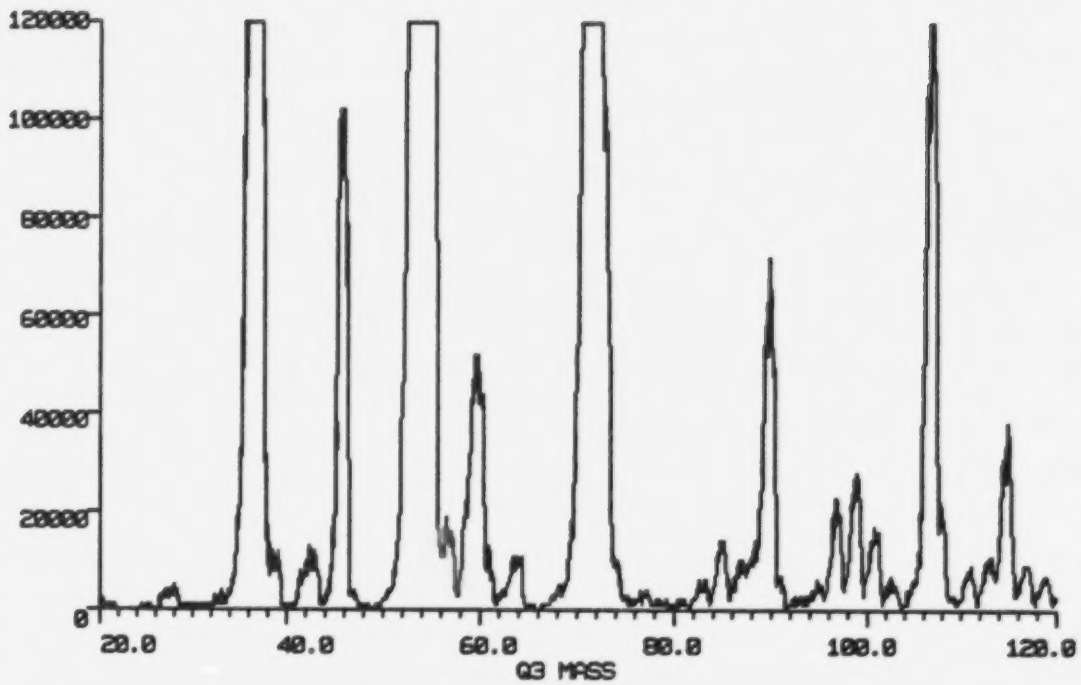

Figure 3A. API/MS Scan of Chamber Prior to Acrylonitrile/NO_x Irradiation.

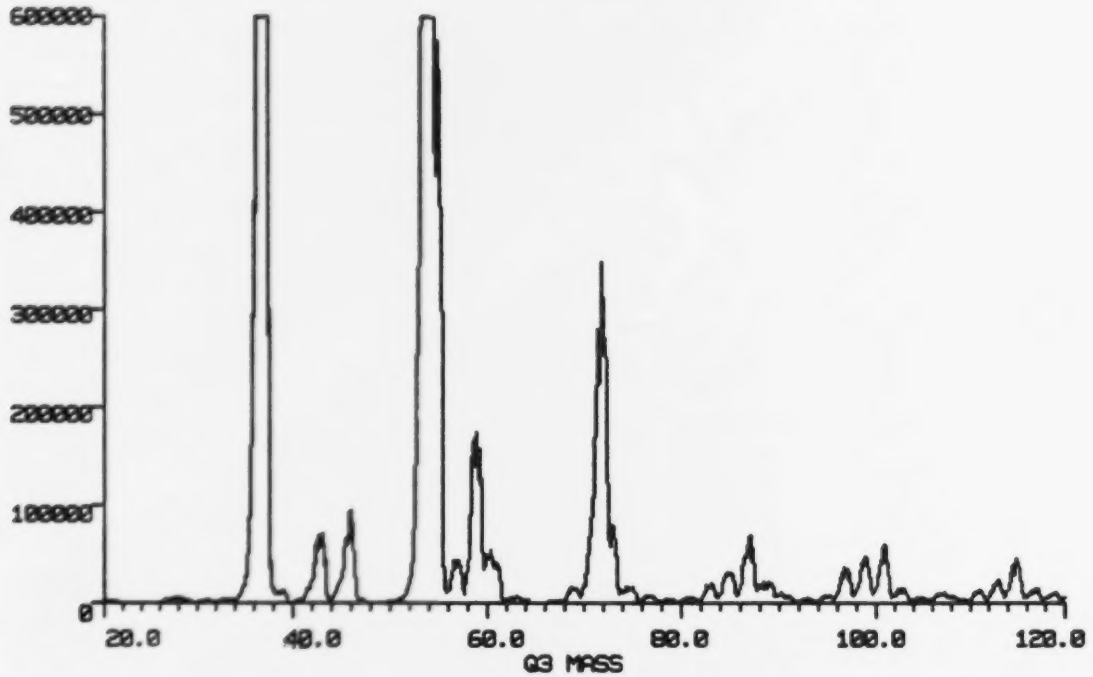

Figure 3B. API/MS Scan of Chamber After 16 Hour Irradiation of Acrylonitrile/NO_x/Air.

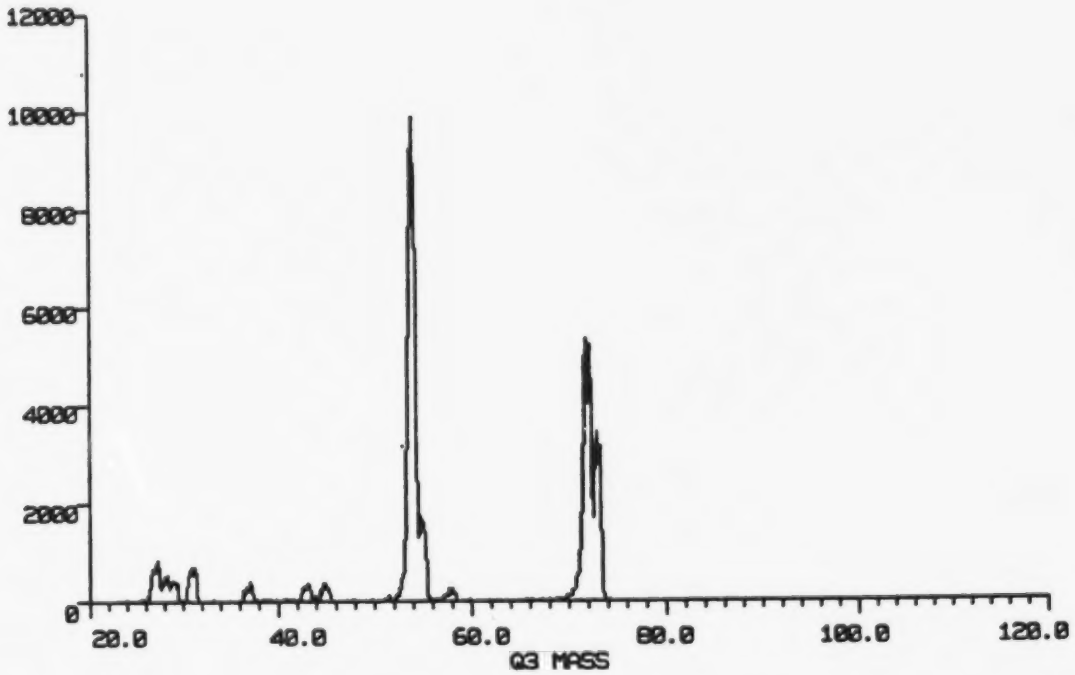

Figure 4. CID Spectrum of m/z 72 Ion Formed in Acrylonitrile/NO_x/Air Irradiation.

products in the experiment just prior to this one. It is possible these peaks represent a carry over from the toluene experiment.

In summary, acrylonitrile was observed to react slowly under conditions conducive to photochemical reaction. Formaldehyde was observed as a reaction product. No other organic products were identified unambiguously, although low levels of PAN or a related compound were produced, and there were small increases in the intensities of several peaks in the API mass spectrum. The CID spectrum of one of these peaks is roughly consistent with the structure of HOC(O)CN, although this identification is extremely speculative and the mechanism for formation of this compound is unclear.

In a study reported after our literature review was completed, Edney et al.[29] found CH_2O, CO and HCN as products of the OH initiated oxidation of acrylonitrile. They also reported an unknown compound which they speculated was formyl cyanide.

Epichlorohydrin

Epichlorohydrin was irradiated for 24 hours at an initial organic/NO_x ratio of 10. As reported for the analogous hydrocarbon, propylene oxide, the photochemical reaction of epichlorohydrin is quite slow. The concentration of total hydrocarbons, as measured by the heated probe FID instrument, decreased at about the same rate as the dilution rate. There was no evidence for aldehyde or dialdehyde production, nor were formyl chloride or carbon monoxide formed. The only potential product identified was acetone, and it appeared in both the MS/MS spectrum and DNPH/HPLC chromatogram. However, because of the ubiquity of acetone in the laboratory, and unlikely formation of acetone from epichlorohydrin, we suspect that the observed acetone increase is artificial.

Under the conditions of this experiment, epichlorohydrin reacted only very slowly, if at all. No organic products were identified by GC, HPLC, or MS/MS.

p-Dichlorobenzene

A mixture of 5 ppm (v/v) p-dichlorobenzene and 0.5 ppm NO_2 in ultrapure air was irradiated for 20 hours in the 17.3 m^3 chamber. The p-dichlorobenzene disappearance rate was only slightly greater than the chamber dilution rate. Only about 64 ppb of O_3 was present after 20 hours of reaction. No monoaldehydes or dialdehydes were observed above the detection limit of approximately 10 ppb.

Atmospheric pressure ionization mass spectrometry was employed to search for reaction products. The chamber air was scanned in both the positive and negative ion modes. Several peaks in the negative ion mode were observed to increase during the experiment. At the end of the experiment, the TAGA instrument was switched to the MS/MS mode of operation. Two of the product peaks were identified as dichlorophenol and dichloronitrophenol. These were the only two organic products identified in the p-dichlorobenzene reaction.

Toluene

Several experiments were carried out with toluene in conjunction with a related EPA Cooperative Agreement (No. 810276, Smog Chamber Study of Aromatic VOC's and Their Oxidation Products). Experiments were initiated with 5 ppm (v/v) toluene and 0.5 ppm NO_2 in clean air. The reports surveyed in the literature review found the following organic products resulting from toluene/NO_x photooxidation: formaldehyde, benzaldehyde, cresols, benzylnitrate, nitrocresols, nitrotoluene, PAN, methyl nitrate and methyl glyoxal.

The toluene reaction products identified in this study are listed in Table 8. Extensive use has been made of the API MS/MS technique, as well as DNPH/HPLC and GC methods. Two sets of API mass spectra, one taken prior to irradiation and the other after five hours of reaction, are shown in Figures 5 and 6. In both sets of figures, a scan of the mass range from 20 to 120 amu is shown in Figure A and from 120 to 220 amu in Figure B. The scale change in the ordinate should be noted.

TABLE 8. TOLUENE REACTION PRODUCTS IDENTIFIED IN THIS STUDY

Formaldehyde
Benzaldehyde
Glyoxal
Methylglyoxal
Peroxyacetyl nitrate
Butenedial*
4-oxo-2-pentenal (acetyl acrolein)*
4-oxo-2-butenoic acid*
4-oxo-2-pentenoic acid (acetyl acrylic acid)*
2-butenal (crotonaldehyde)*
Nitrotoluene*
o-Cresol**
2-butenoic acid (crotonic acid)*
Nitrocresol*
Benzylnitrate*

* Tentative identification based on MS/MS dissociation pattern.

** Identified by GC in previous experiments.

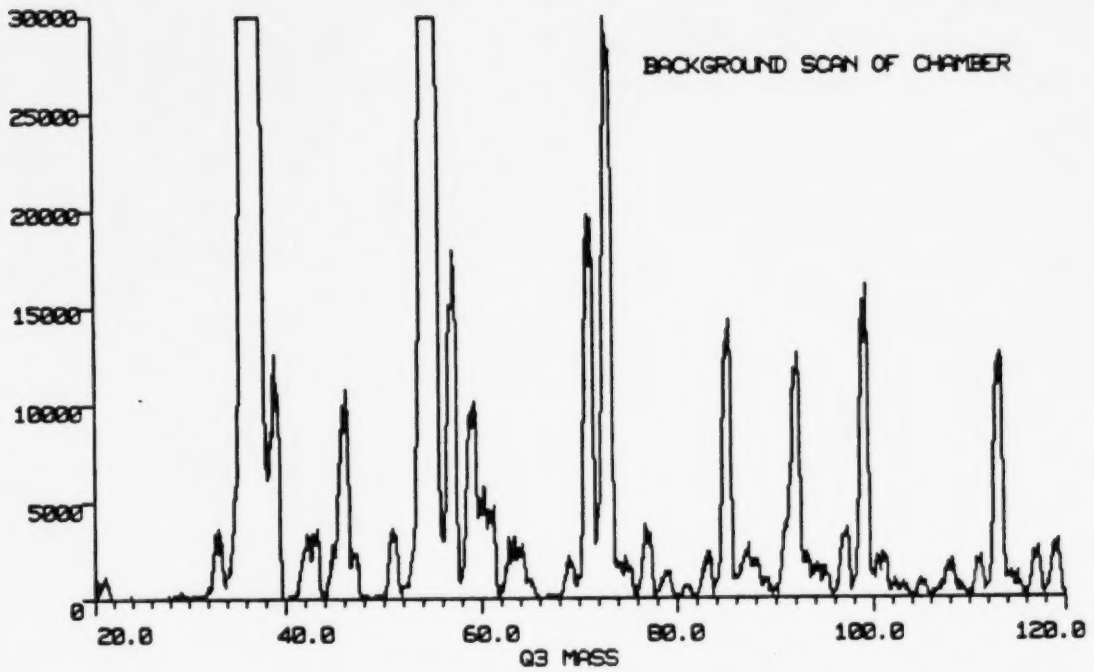

Figure 5A. API Mass Spectrum of Toluene/NO_x/Air Mixture Prior to Irradiation.

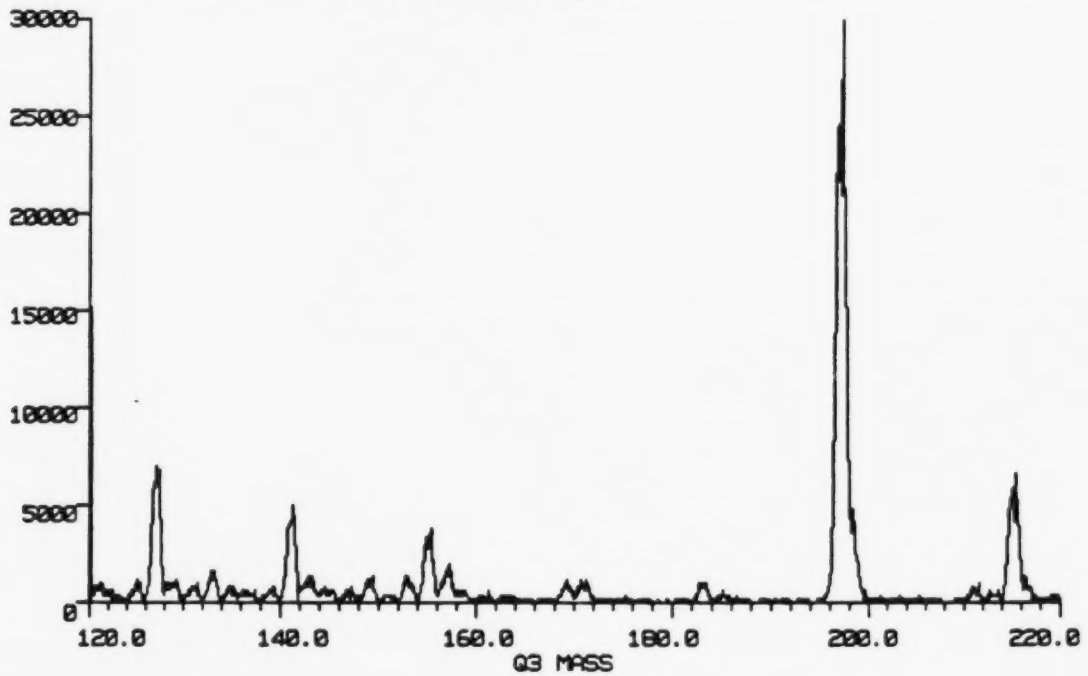

Figure 5B. API Mass Spectrum of Toluene/NO_x/Air Mixture Prior to Irradiation.

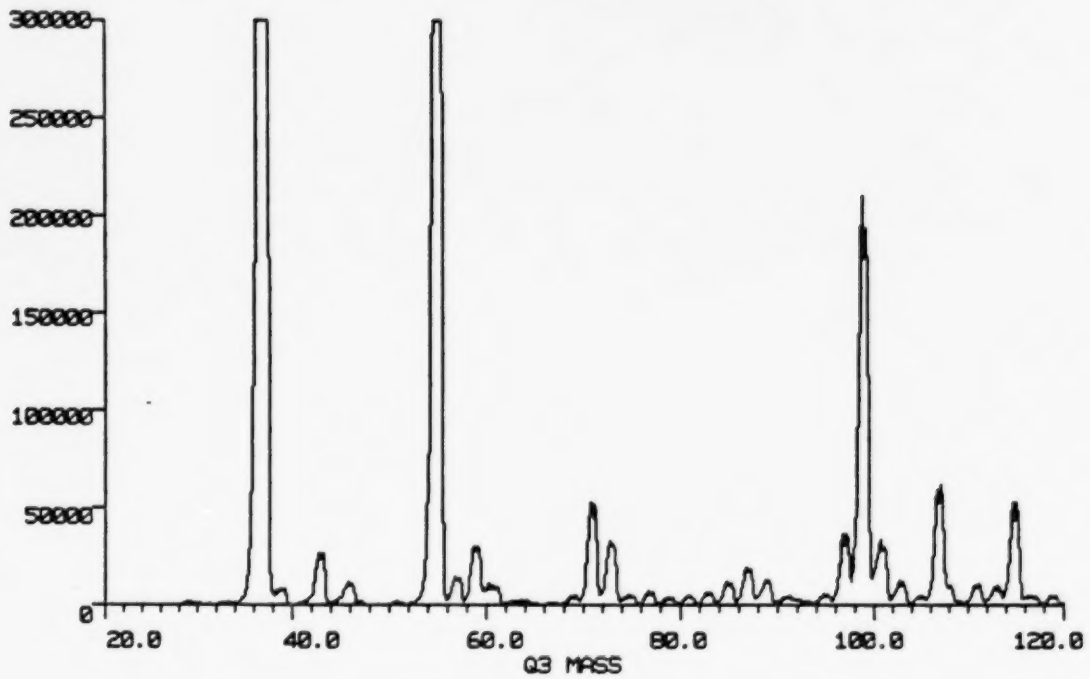

Figure 6A. API Mass Spectrum of Toluene/NO_x/Air Mixture After Five Hours of Reaction.

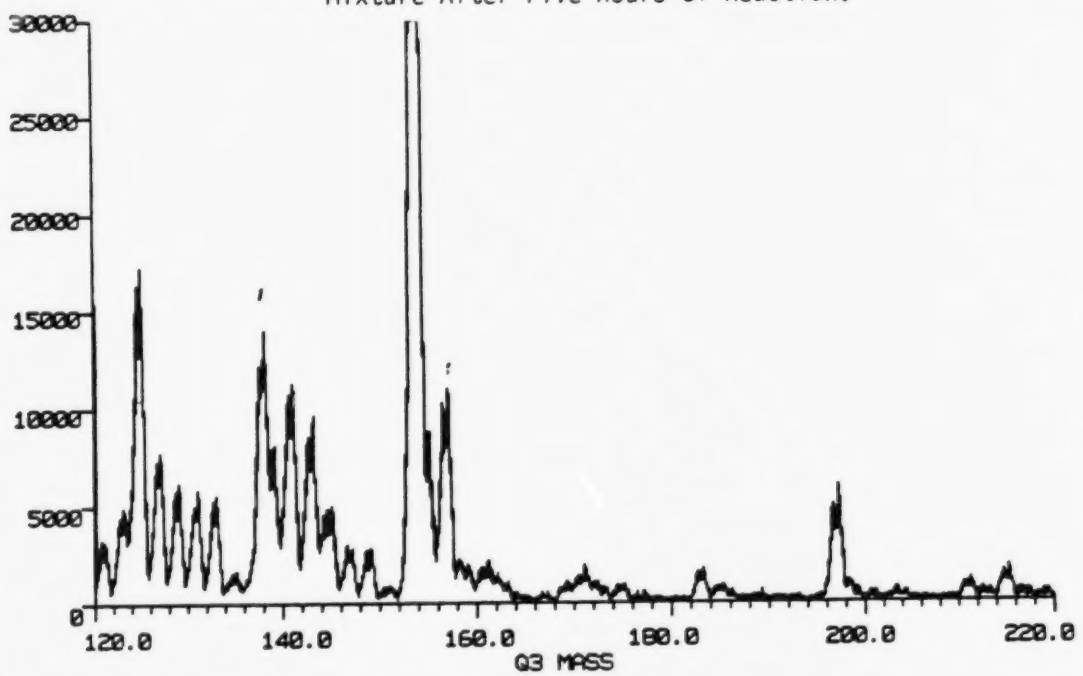

Figure 6B. API Mass Spectrum of Toluene/NO_x/Air Mixture After Five Hours of Reaction.

These figures show significant increases in several peaks, including those at m/z 99, 107, 115 and 154. The peaks at m/z 99 and 115 were tentatively identified by their fragmentation pattern in the MS/MS mode as acetyl acrolein and acetyl acrylic acid. These compounds were subsequently synthesized and introduced into the TAGA instrument to obtain an MS/MS spectrum for comparison with that obtained in the toluene experiments. Comparison of the fragmentation pattern (CID) of the unknown toluene product at m/z 99, with the pattern for acetyl acrolein is shown in Figure 7. A similar comparison for acetyl acrylic acid is shown in Figure 8. In both cases, the agreement is excellent.

Other peaks which increased during the toluene/NO_x irradiation may be found in Figures 5 and 6. Peaks at m/z 107 and 154 were examined by MS/MS at the conclusion of the smog chamber experiment. The MS/MS dissociation patterns of the compounds at m/z 107 and 154 are shown in Figures 9 and 10 respectively. The dissociation patterns lead to tentative identification of these compounds as benzaldehyde and nitrocresol. Comparative spectra of authentic compounds were not taken due to the limited availability of the TAGA. However, benzaldehyde was also identified by GC and DNPH/HPLC in the toluene experiments.

Profiles of the concentrations of many of the products observed during a toluene experiment are shown in Figure 11 A-D. Initial concentrations were 1.6 ppm (v/v) toluene, 0.23 ppm NO and 0.25 ppm NO_2. The peak heights shown in Figure 11D are from the API mass spectra. Identifications shown in parenthesis in Figure 11D are tentative, and are based on the MS/MS dissociation patterns, as discussed earlier.

Subsequent to the completion of this study and presentation of the preliminary results[30], two quite pertinent reports of toluene's atmospheric reaction products have been published. O'Brien et al.[31] used direct probe MS/MS to examine the wash from the walls of 22 liter Pyrex vessels in which 1-10 ppm of toluene and NO_x had reacted. Their identification of methyl glyoxal and 4-oxo-2-pentenal is consistent with the results of this study. They also identified 5-oxo-1,3-hexadiene, hydroxy-4-oxo-1,3-hexadiene, hydroxy-4-oxo-2-pentenal, and hydroxy-2-

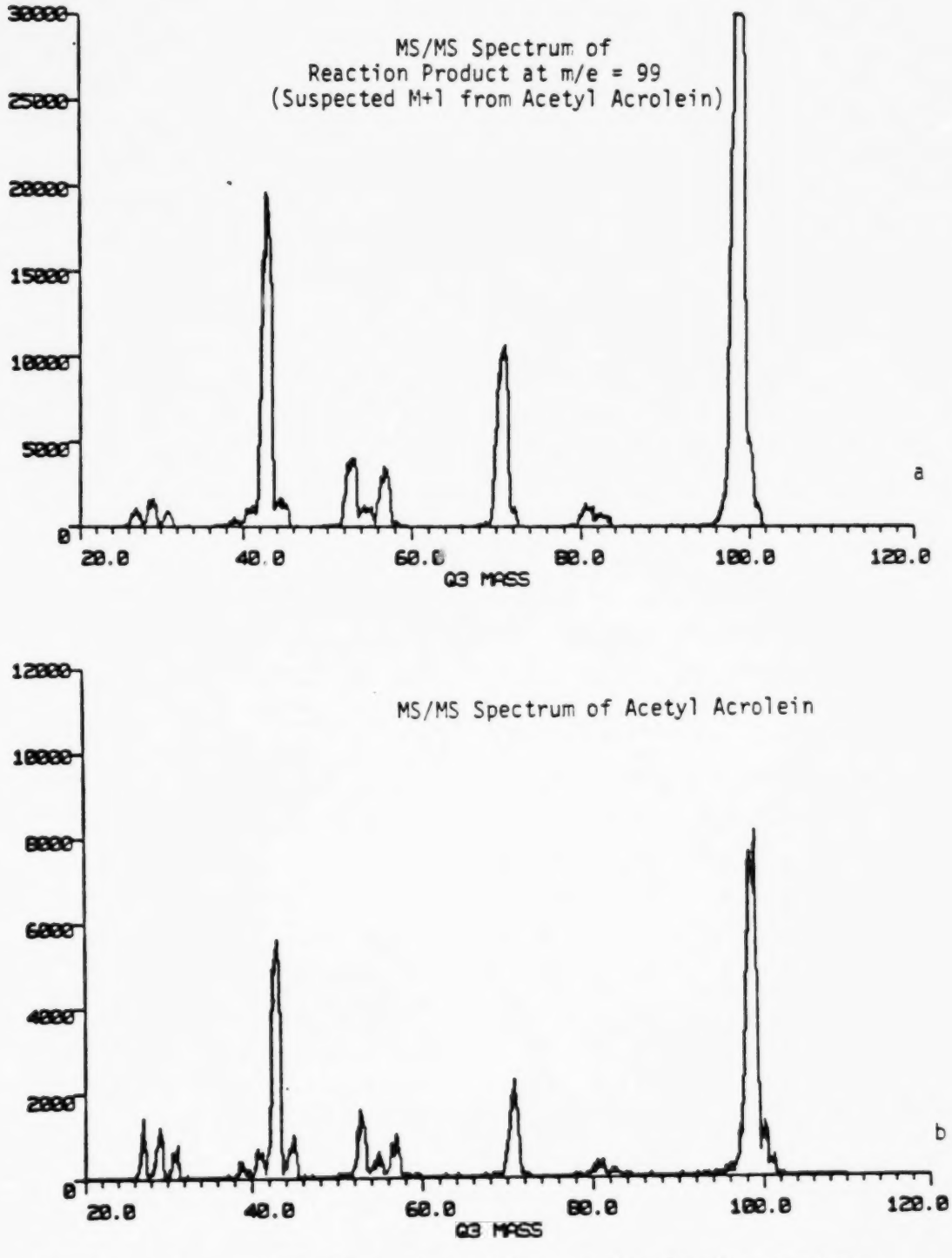

Figure 7. Comparative CID Spectra of Smog Chamber Reaction Product (parent mass of 98).

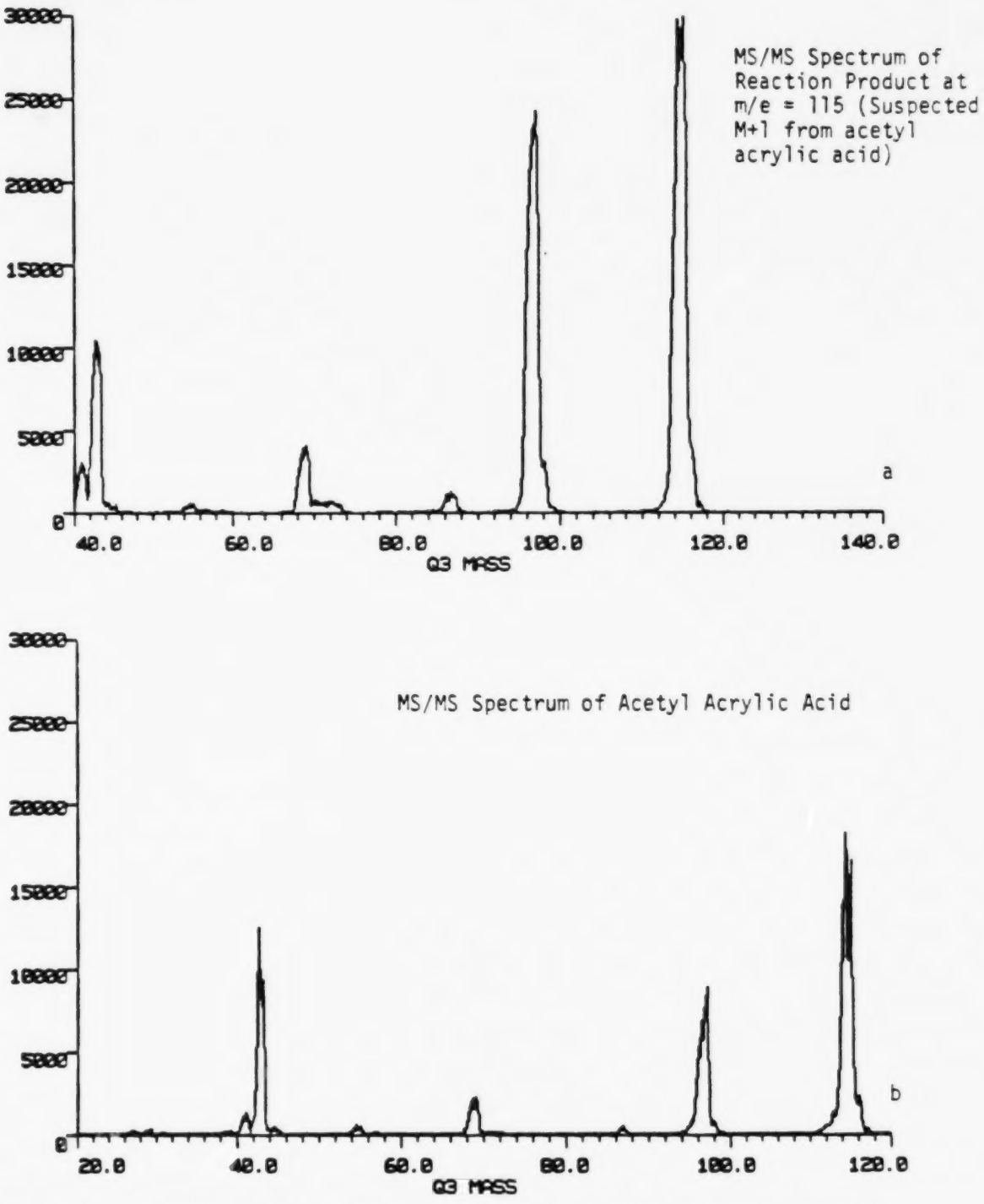

Figure 8. Comparative CID Spectra of Smog Chamber Reaction Product (parent mass of 114).

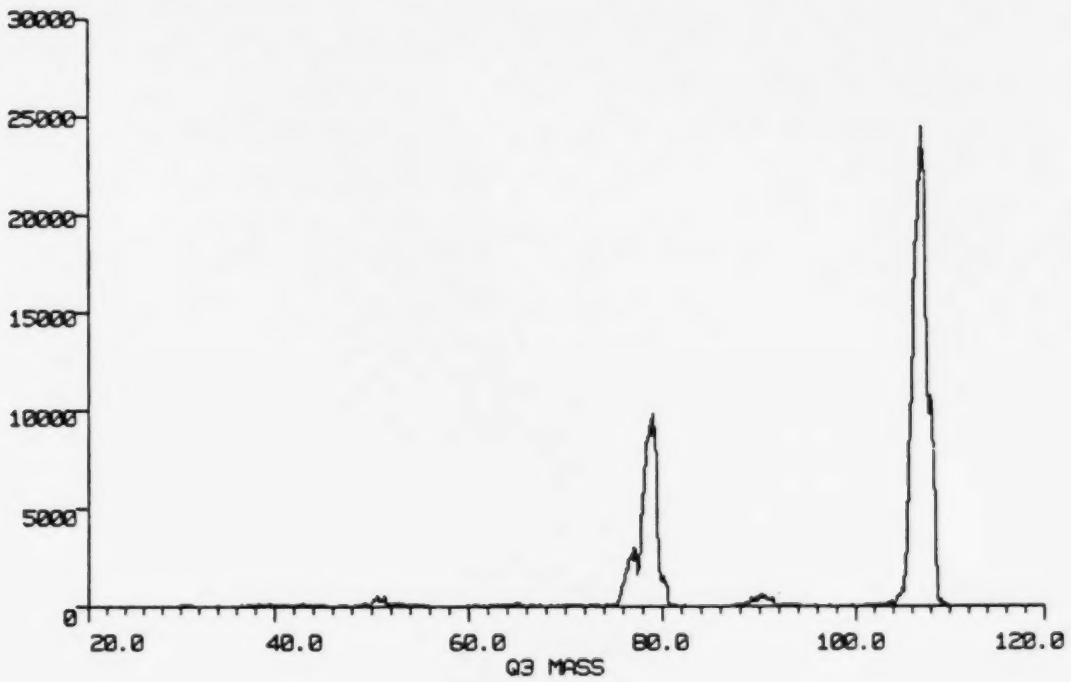

Figure 9. Collisionally Induced Dissociation (CID) Pattern of Compound at m/z 107 from Toluene/NO_x/Air Irradiation.

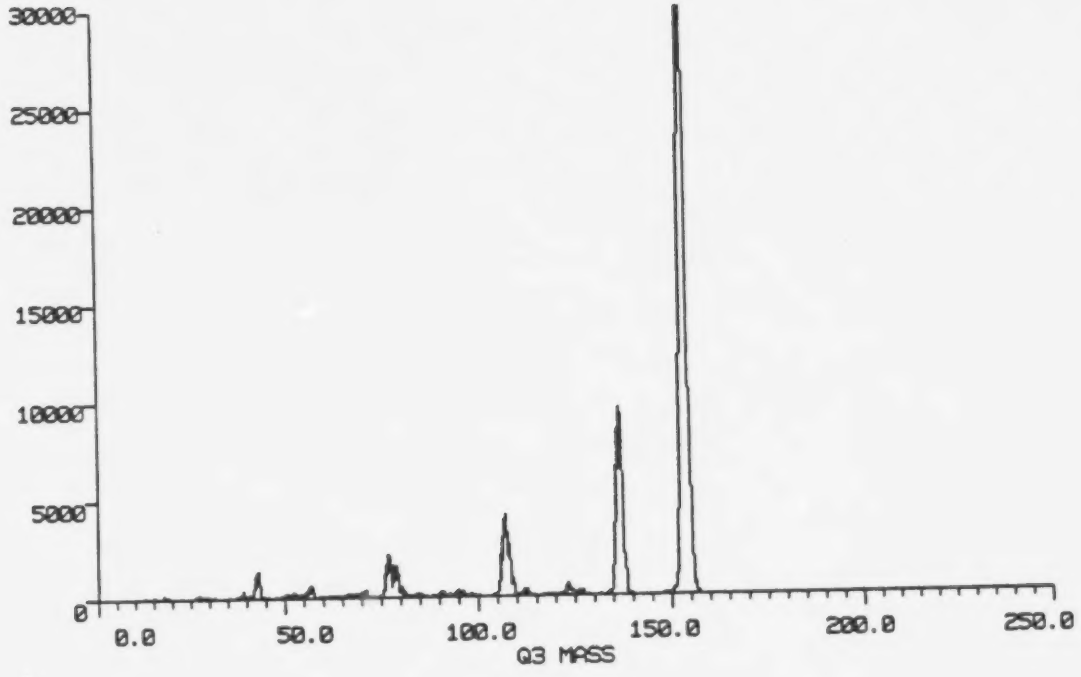

Figure 10. Collisionally Induced Dissociation (CID) Pattern of Compound at m/z 154 from Toluene/NO_x/Air Irradiation.

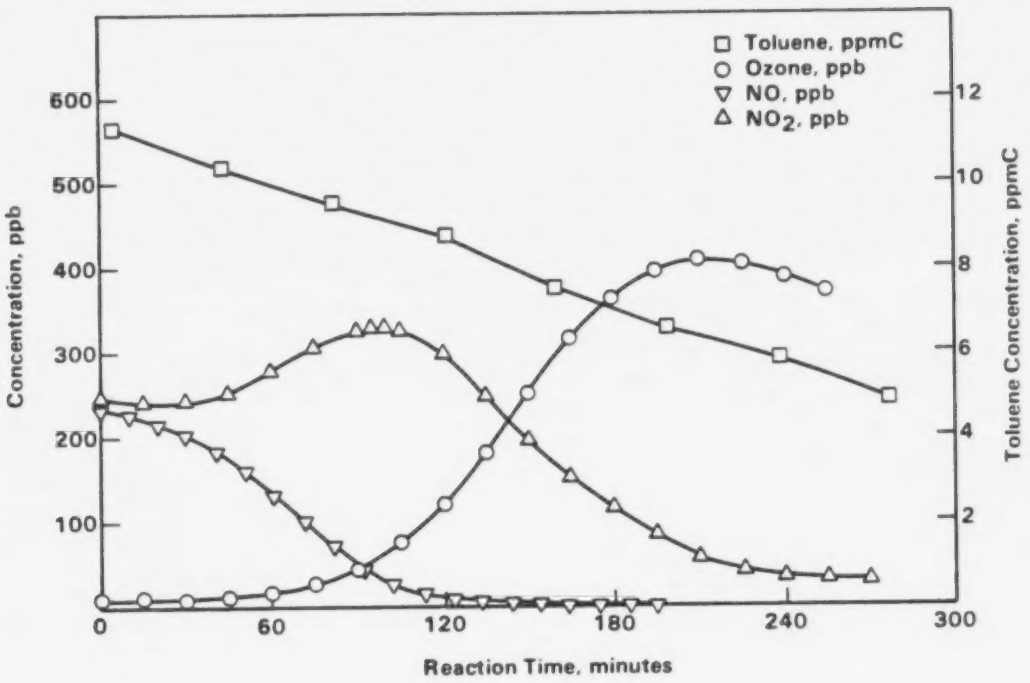

Figure 11A. Profiles from Toluene/NO_x Irradiation in 17.3 m^3 Smog Chamber.

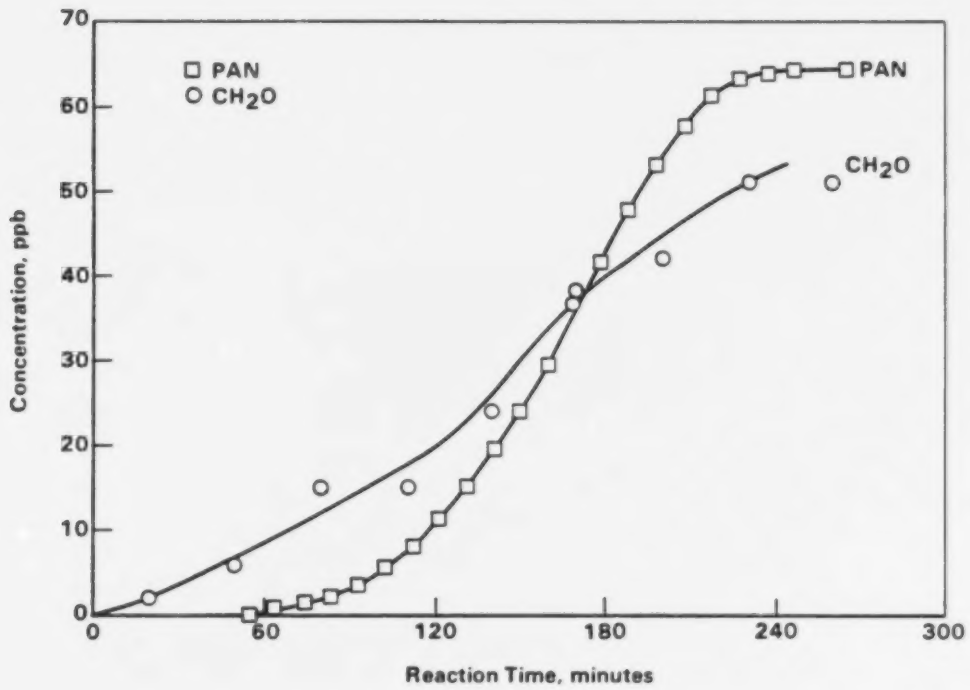

Figure 11B. Profiles from Toluene/NO_x Irradiation in 17.3 m^3 Smog Chamber.

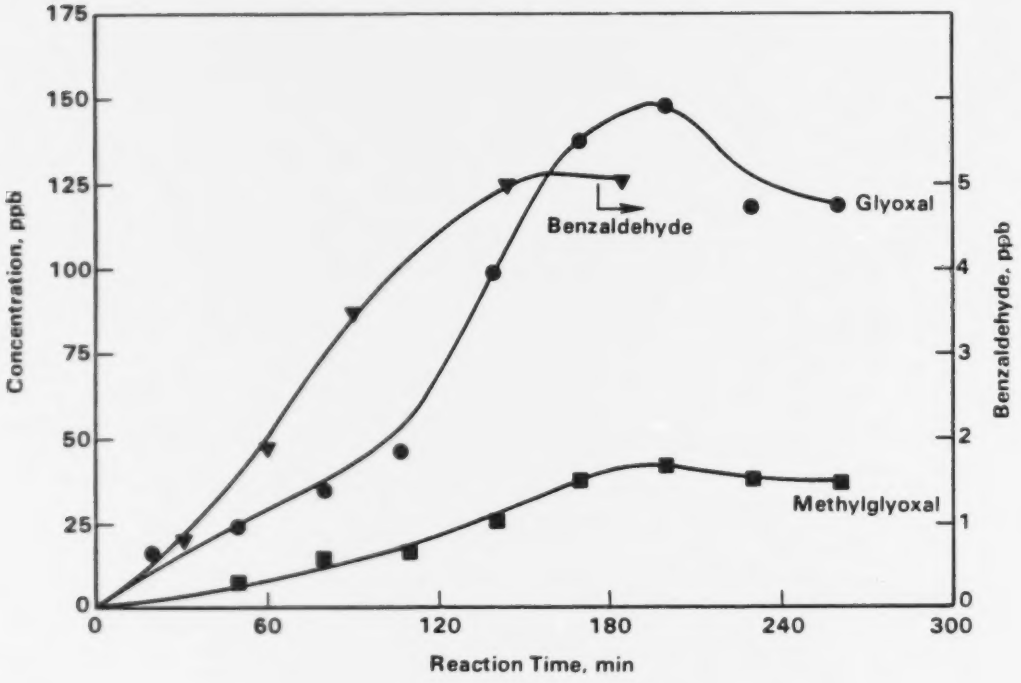

Figure 11C. Profiles from Toluene/NO_x Irradiation in 17.3 m^3 Smog Chamber.

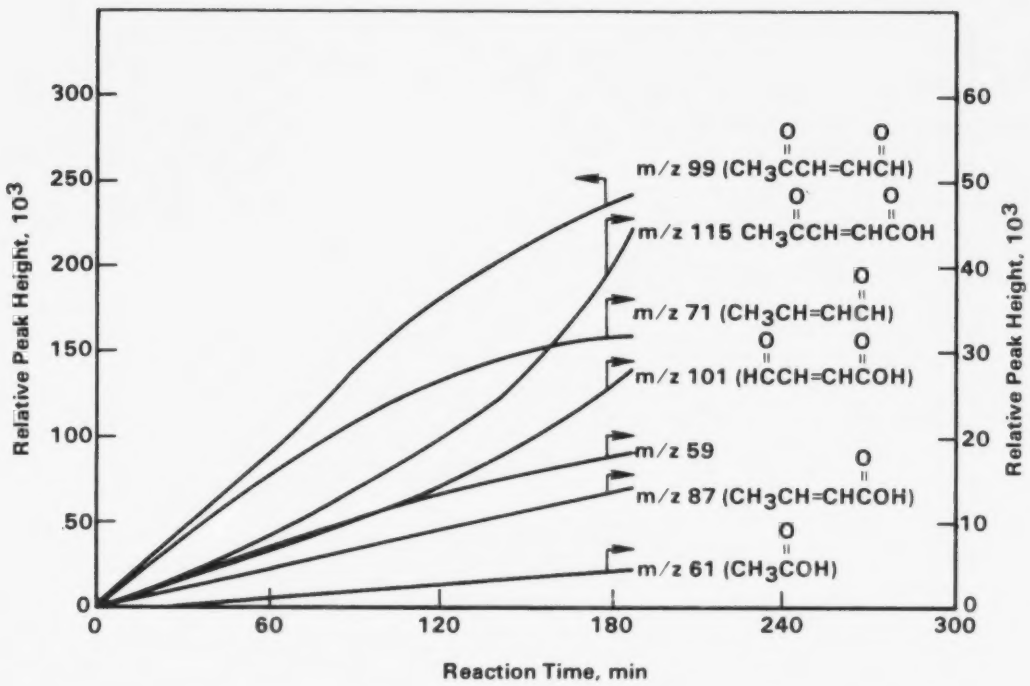

Figure 11D. Profiles from Toluene/NO_x Irradiation in 17.3 m^3 Smog Chamber.

butenedial. These latter two compounds are alternative identifications for the product peaks we have reported as 4-oxo-2-pentenoic acid (acetyl acrylic acid) and 2-butenoic acid. Our assignment is based on the similarity of the unknown compound's CID spectrum with the spectrum of an actual sample of acetyl acrylic acid (Figure 8). However, until a CID spectrum of hydroxy-4-oxo-2-pentenal is available for comparison, the question of whether these compounds are acids or hydroxy aldehydes can not be answered definitively.

Shepson et al.[32] reported several toluene reaction products based on GC/MS and HPLC analyses of samples from toluene/CH_3ONO/NO/air irradiations in Teflon bags. In addition to several compounds already noted, they observed 4-pentene-2,3-dione, furan, 2-methyl furan, furfural, 1-butene-3-one, and 2-oxo-3-butenal. These compounds may represent several of the unidentified product peaks shown in Figure 6.

Benzene

Benzene is a carcinogen of known low photochemical reactivity. As noted in Table 7, previous studies have reported nitrobenzene, nitrophenol, dinitrophenol, and phenol as major products. In this study, 5 ppm benzene and 0.5 ppm NO_2 were irradiated in clean air for 22 hours in the 17.3 m^3 smog chamber. After seven hours of irradiation, approximately 225 ppb NO_2 was added to the chamber to continue the reaction overnight.

During the first 6-8 hours of reaction, benzene disappeared at essentially the same rate as dilution, and very little O_3 or PAN was observed. After the injection of NO_2 seven hours into the experiment, O_3 and PAN increased and the rate of benzene disappearance increased to a value 0.018 hr^{-1} above dilution.

Ozone and PAN both reached maximum values after 10-11 hours of reaction. The maximum O_3 concentration was 253 ppb, while PAN maximum was 17.7 ppb. There was evidence in the API mass spectral data for phenol, nitrobenzene, and nitrophenol. However, these were not identified unambiguously. There was also evidence for glyoxal and butenedial, and later in the

experiment, 4-oxo-2 butenoic acid, which may be produced from butenedial. However, neither glyoxal nor any other aldehyde or dialdehyde was present above the detection limit of the DNPH/HPLC procedure (~10 ppb) after 22 hours of reaction. It may be that the aldehydes and dialdehydes produced in the initial stages of the reaction were lost to secondary reactions and dilution by the time the 22 hour DNPH sample was collected.

Aniline

Five hazardous air pollutants were added to the list of compounds to undergo product screening studies after the literature survey was completed. These compounds are aniline, nitrobenzene, chlorobenzene, phenol, and o-cresol. Because these compounds are likely to have very low photochemical reactivity, a different approach was used to investigate their reactions. Each of these five compounds was irradiated in the 17.3 m^3 chamber in the presence of NO_2 and the EKMA hydrocarbon mixture. The concentrations employed were as follows:

1 ppm (v/v) test compound
1 ppm (v/v) propylene
3 ppm (v/v) butane
0.4 ppm NO_2.

The API MS/MS was unavailable for these runs, so a GC/MS was employed for mass spectral identification of reaction products. The experiments were designed assuming 20 percent conversion over an eight hour irradiation and a one liter cryosample for the GC/MS. With a 10 ng detection limit for the GC/MS, these conditions should permit detection of products at levels as low as two percent of the reacted test compound.

Initial experiments were performed with the propylene/butane mixture and NO_2 alone, in order to define the baseline reactivity and reaction product conditions. Subsequent experiments were then carried out with this mixture in the presence of aniline and the other HAPs. Plots of the concentrations of O_3, NO_2, and PAN for the two experiments with and without aniline are included in Figure 12 A and B. The dramatic decrease in O_3 and PAN when aniline is present illustrates the inhibitory effects

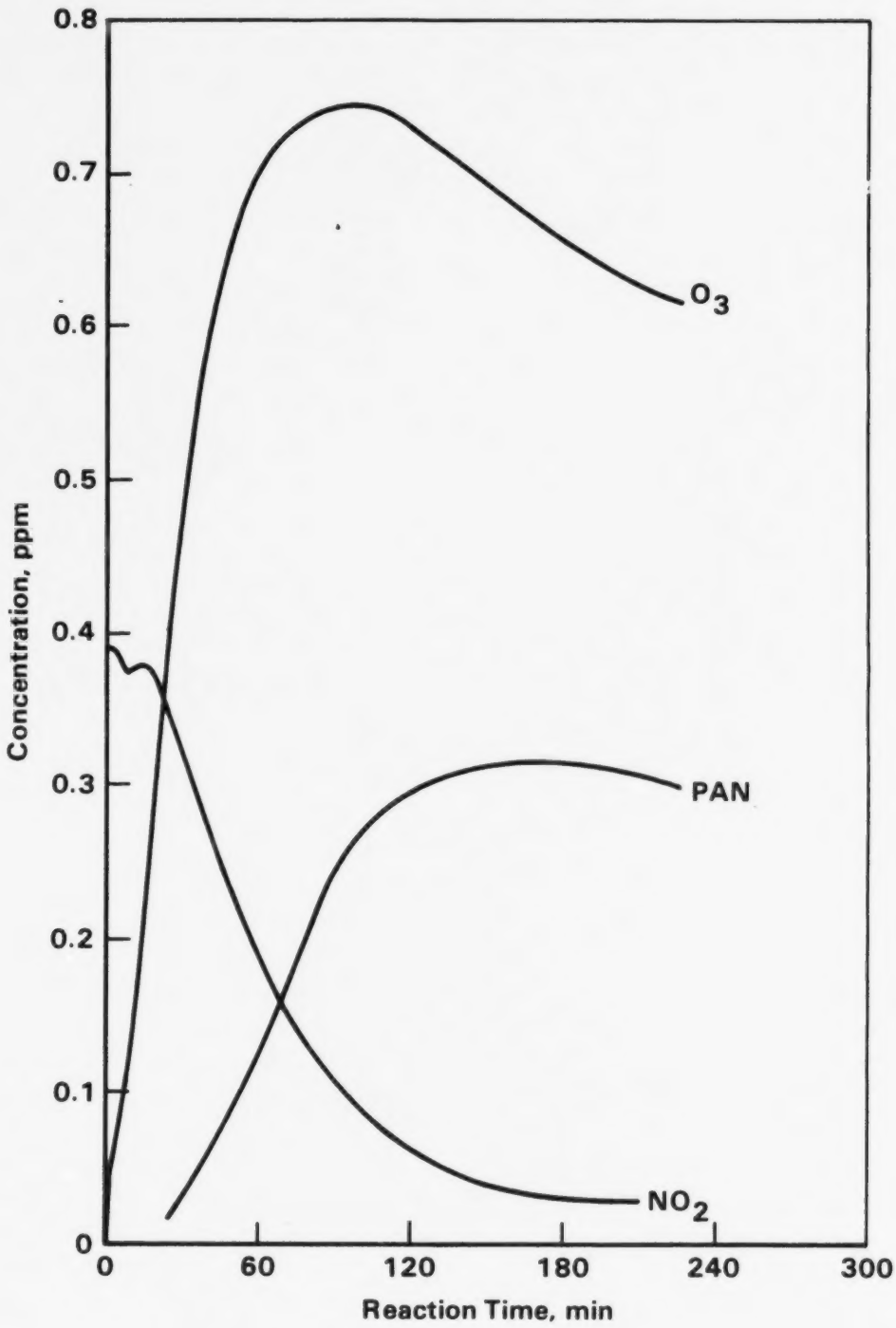

Figure 12A. Concentration Profiles from Propylene/Butane/NO_2 Irradiation.

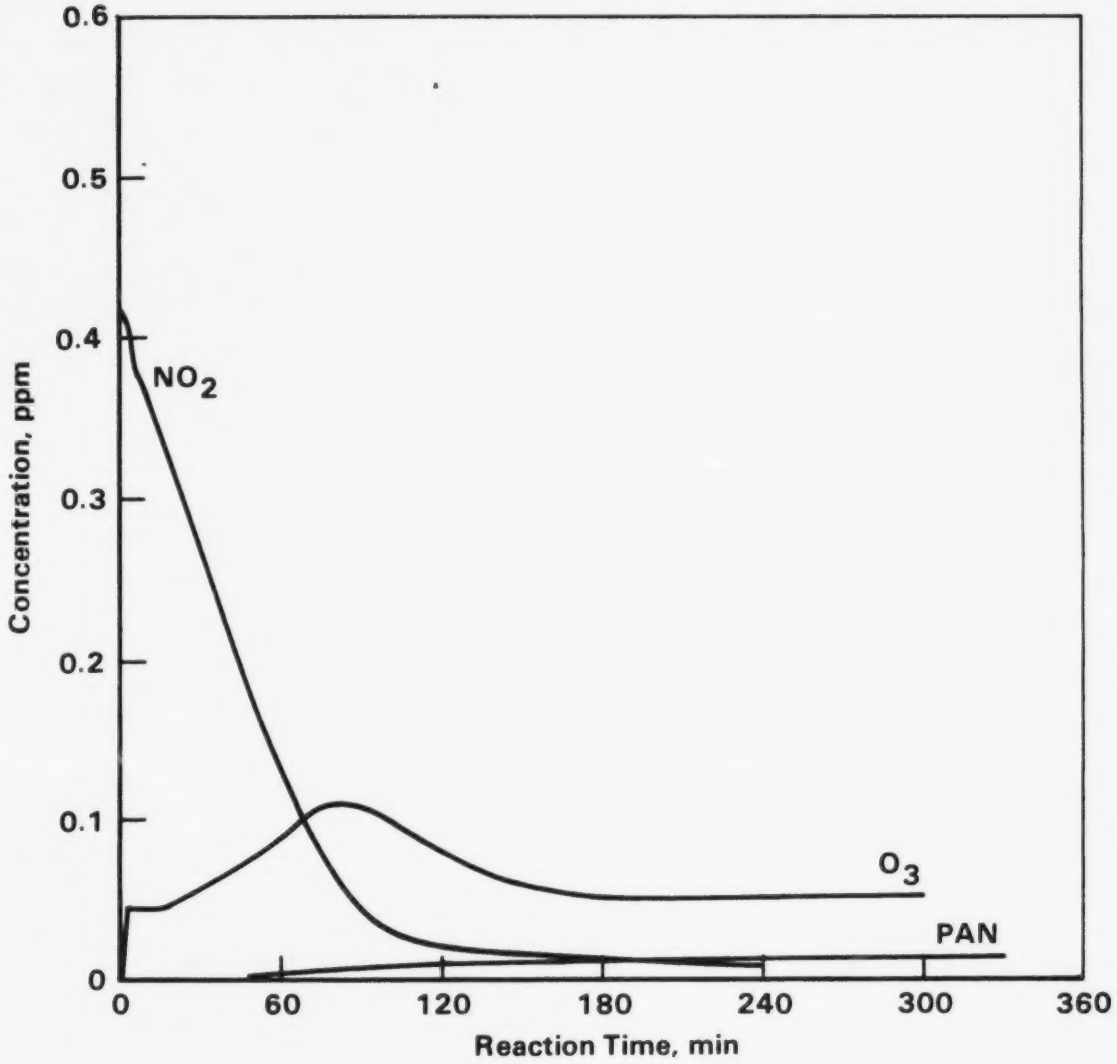

Figure 12B. Concentration Profiles from Aniline/Propylene/ Butane/NO_2 Irradiation.

of aniline reported earlier[33,34]. The results for formaldehyde and acetaldehyde shown in Figure 13 also convey the inhibitory influence of aniline. The concentrations of both aldehydes are reduced significantly when aniline is present. The dialdehydes, glyoxal and methylglyoxal, are produced at low concentrations in the baseline experiment with propylene and butane, and are also reduced when aniline is present. Production of methyl glyoxal is almost completely inhibited.

The rates of disappearance of the organic species followed first order kinetics. The rates determined from specific GC measurements were:

Compound	Disappearance Rate, Hr^{-1} (corrected for dilution)
Butane	0.006
Propylene	0.119
Aniline	0.660

The ratio of the aniline to butane disappearance rate is 110. Assuming that reaction with hydroxyl radical is the main chemical loss process for both species, the ratio of literature rate constants for OH reaction ranges from 9-45, depending on the value selected for reaction with aniline. This comparison suggests that aniline disappears at least twice as fast as would be predicted if reaction with OH were the only removal mechanism.

A great deal of particulate material was produced in the experiment with aniline, as reported previously[34]. After three hours of reaction, the light scattering aerosol level (b_{scat}) was 58 x $10^{-4}m^{-1}$. At the end of the experiment the chamber air was sampled through a preweighed high purity quartz fiber filter. The collected particulate material was an intense yellow-brown color. The mass collected corresponds to an aerosol phase concentration of 285 ug/m^3 at the end of the experiment, which in turn corresponds to approximately 12 percent of the reacted aniline. It is probable that a considerable amount of aerosol generated during the experiment was lost by deposition to the chamber surfaces during the

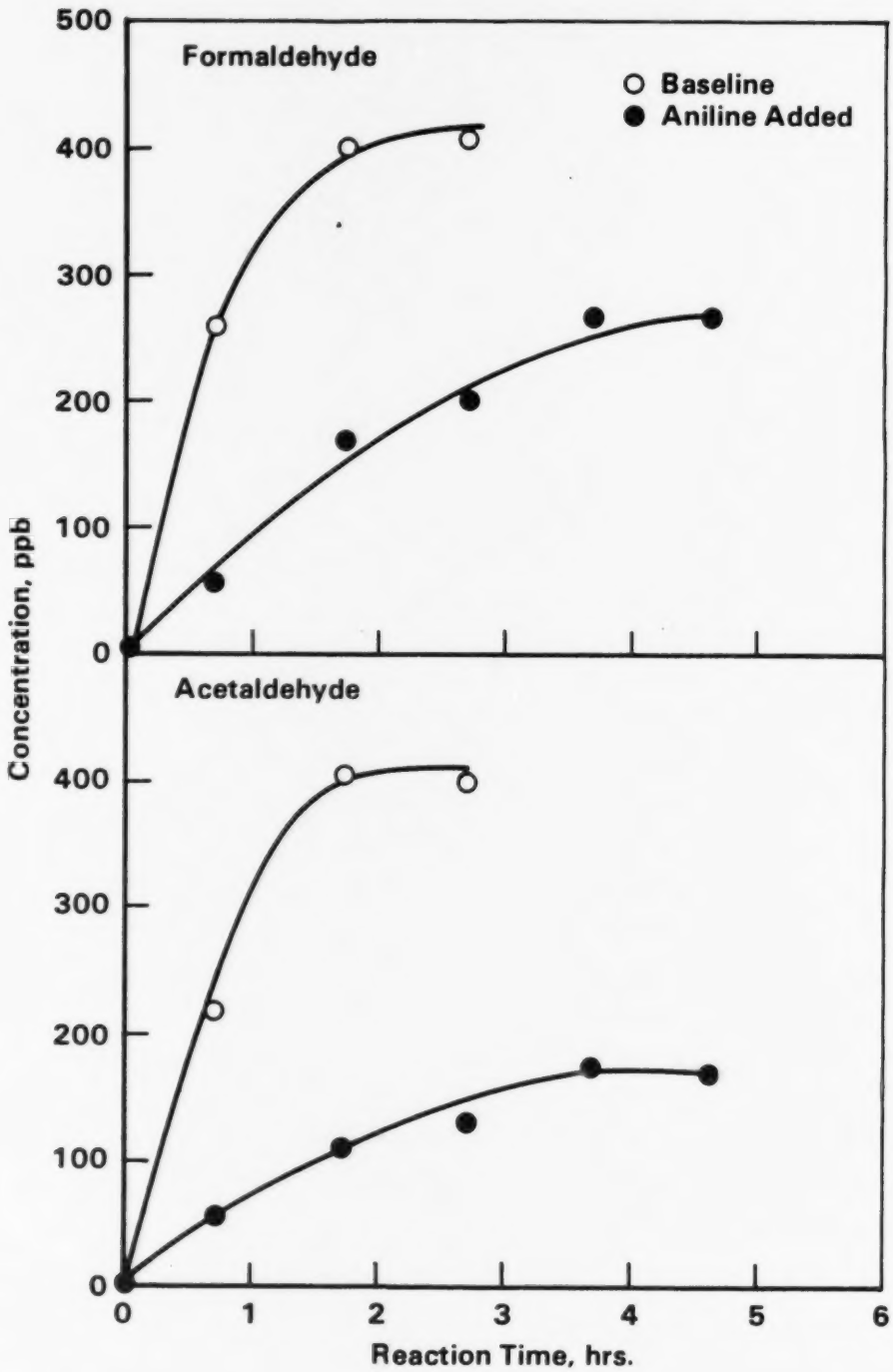

Figure 13. Concentration Profiles of Formaldehyde and Acetaldehyde from Propylene/Butane/NO_2 Experiments With and Without Added Aniline.

five hour reaction, so the actual percentage of reacted aniline attributable to particulate material may be considerably greater than 12 percent.

As noted earlier, the concentrations of the organic products formaldehyde, acetaldehyde, glyoxal, methyl glyoxal, and PAN were reduced when aniline was present in the chamber. No new mono- or dialdehydes were observed in the aniline experiment by the DNPH/HPLC procedure. No products were detected in the chromatographic output from the cryogenic capillary column FID/GC. An unidentified reaction product was observed to elute between the O_2 and PAN peaks on the electron capture detection GC. The area of this peak followed the same time profile as PAN.

The GC/MS system was used to search for gaseous aniline reaction products by cryogenic sampling of the chamber during the experiment. This system was also employed to analyze the extract from the quartz filter aerosol collection. An automated computer search was used to identify the GC/MS peaks by spectral matching techniques. Gas phase products which were tentatively identified by GC/MS include nitrobenzene, nitrophenol, and nitrosobenzene.

A number of compounds appeared in the GC/MS analysis of the filter extract from the aniline experiment. Many of the compounds appear to be contaminants in the original aniline or reaction products of contaminants. The list of computer-identified species includes aniline, nitroaniline, phenol, isocyanato benzene, hydroxy benzonitrile, and N-phenyl formamide. The formation mechanism of the last three compounds is very uncertain, but the presence of N-phenyl formamide in the extract was confirmed by HPLC. This was the major peak in the GC/MS analysis, and its concentration was estimated to be 0.7 ppb from the HPLC results. The most likely formation mechanism seems to be reaction of aniline or an aniline product with formaldehyde either in the gas phase or on the filter.

The filter sample extract was analyzed by GC/MS and by HPLC. The HPLC chromatogram is shown in Figure 14A. A number of significant peaks are observed. The compounds responsible for these peaks must be of low volatility (because they were present in the particle phase), must be

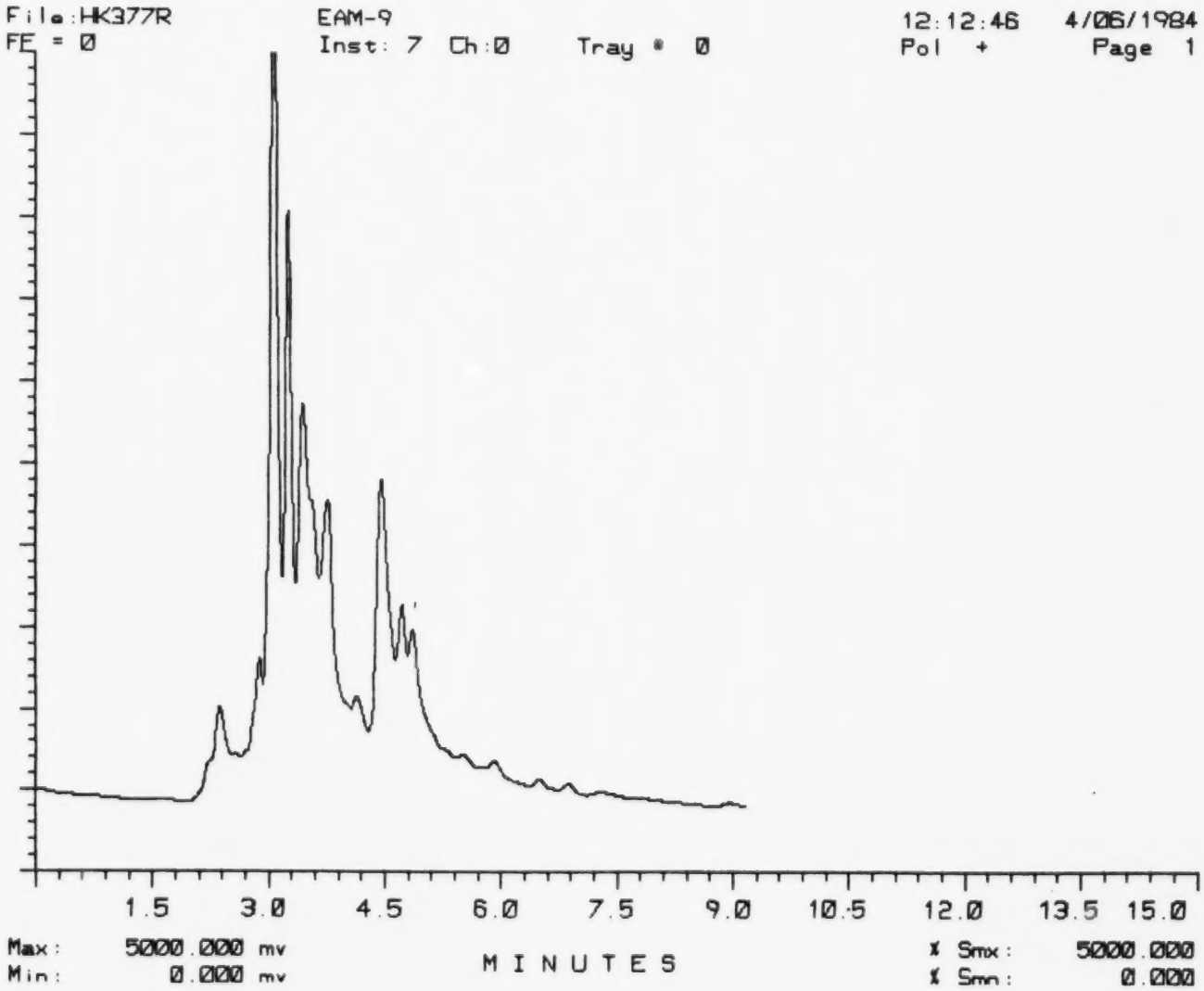

Figure 14A. HPLC Chromatogram of Filter Extract from Aniline Experiment.

amenable to the HPLC analysis conditions, and must be electrochemically active. The peak at a retention time of 4.80 min. appears at the location of benzidine. An authentic sample of benzidine run under the same conditions is shown in Figure 14B. Benzidine is a known carcinogen so the possibility that it may be generated from aniline is of concern. The identification of benzidine is very tentative and the mechanism for its formation in air is unclear, although it is a significant coupling product formed during electrochemical oxidation of aniline. However, even if it were produced in the chamber experiment, that does not mean that it would be formed under atmospheric conditions. Benzidine formation would necessarily require that two aniline molecules/radicals react together, and the possibility of this occurring at the low aniline levels present in the atmosphere is much lower than in a smog chamber containing 1 ppm of aniline.

The other chromatographic peaks in Figure 14A are likely to be aminophenols and/or nitroanilines, but these identifications are only speculative, based on the criteria noted earlier for compounds to appear under these analysis conditions. Further work will be required to identify these aniline reaction products.

Nitrobenzene

One ppm (v/v) of nitrobenzene was irradiated for 5.5 hours in the presence of the propylene/butane/NO_2 mixture in the 17.3 m^3 chamber following the same protocol used for aniline. The maximum ozone concentration was slightly reduced compared to the baseline experiment without nitrobenzene. The maximum PAN concentration was also reduced somewhat. The experiment with nitrobenzene produced similar levels of formaldehyde, acetaldehyde, glyoxal, methylglyoxal, and carbon monoxide as the baseline experiment in the absence of nitrobenzene.

Nitrobenzene was consumed during the experiment at a rate approximately 0.02 hr^{-1} beyond the dilution rate. Thus its lifetime under conditions of this experiment would be about 50 hours, or 4-5 days in the atmosphere (assuming 12 hours of sunlight per day).

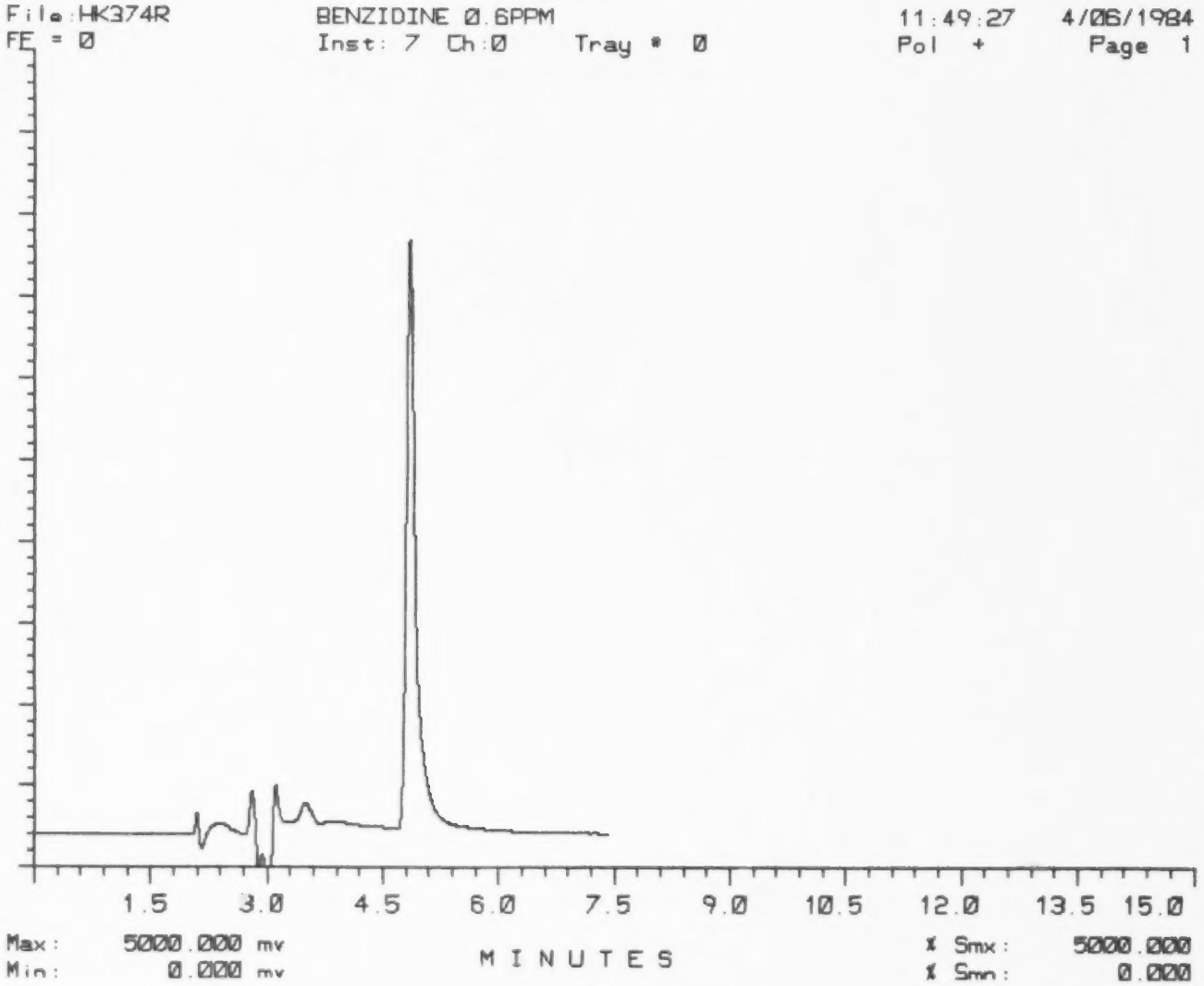

Figure 14B. HPLC Chromatogram of Benzidine Under the Same Conditions As the Chromatographic Run in Figure 14A.

No nitrobenzene reaction products were identified from the direct GC/MS analysis of the reaction mixture. The amount of particulate matter produced in the nitrobenzene experiment was of the same order as the baseline experiment, so the contribution of reaction products in the aerosol phase appears to be negligible.

At the end of the nitrobenzene run, a 60 l impinger sample was collected in 0.1 N NaOH for determination of phenolic compounds. Four peaks were observed in the HPLC chromatogram. A similar collection was made after the baseline experiment and no peaks were observed. Therefore, these peaks represent compounds which are attributable to nitrobenzene reactions. Two of the peaks appeared at retention times consistent with 2-nitrophenol and 4-nitrophenol. The other two species have not been identified.

Chlorobenzene

Chlorobenzene was studied in the same manner as aniline and nitrobenzene. A mixture of 1 ppm chlorobenzene, 1 ppm propylene, 3 ppm butane, and 0.4 ppm NO_2 was irradiated for five hours in the 17.3 m^3 chamber. Chlorobenzene degradation was monitored by capillary column GC. The reacting mixture was screened for reaction products using FID/GC, ECD/GC, GC/MS, DNPH/HPLC and an HPLC method for phenolic products.

Chlorobenzene disappeared essentially at the same rate as dilution, indicating that the compound did not react to any appreciable extent under the conditions of this experiment. The presence of chlorobenzene in the mixture seemed to have little effect on the formation of O_3, PAN, formaldehyde, acetaldehyde, glyoxal, methyl glyoxal or butanal. Production of particles in the light scattering size range was negligible.

At the conclusion of the chlorobenzene experimental, a NaOH impinger sample was collected and analyzed by HPLC for phenolic compounds. No peaks were observed.

O-Cresol

Ortho-cresol was irradiated in mixture with propylene, butane, and NO_2 and the chamber contents analyzed for photochemical reaction products.

As for previous experiments, 1 ppm (v/v) of o-cresol was irradiated in the presence of 1 ppm propylene, 3 ppm butane, and 0.4 ppm NO_2 in ultra-clean air in the 17.3 m^3 chamber. As in the case of aniline, o-cresol had a significant inhibitory effect on production of photochemical oxidants. The maximum O_3 and PAN concentrations were reduced to less than one half of the levels formed in the absence of o-cresol. The peak levels of formaldehyde, acetaldehyde, glyoxal, and methyl glyoxal were also reduced by approximately 50 percent.

o-Cresol was removed at a rate of 0.21 hr^{-1} beyond the dilution rate, which suggests an atmospheric lifetime of about five hours under photochemically active conditions. Significant levels of light scattering aerosol particles were produced during the experiment. The b_{scat} maximum reached 33 x 10^{-4} m^{-1} within the first two hours of reaction. The mass of material collected on a quartz filter at the end of the experiment corresponded to approximately seven percent of the reacted o-cresol. Because particulate material was undoubtedly lost to the chamber walls during the experiment, the fraction of reacted o-cresol which formed aerosol must be greater than seven percent.

Several reaction product peaks were observed to increase during the experiment according to the GC/FID measurements. Attempts to identify the species responsible for these peaks made use of the GC/MS capability. The only new product observed by GC/MS was 2-hydroxy benzaldehyde.

Three hours into the o-cresol experiment a NaOH impinger sample was collected and analyzed by HPLC for phenolic compounds. Three peaks were observed in the chromatogram, with the major peak identified as residual o-cresol. GC and HPLC measurements of o-cresol at the time of this sample agreed within 15 percent. The two phenolic reaction product peaks were tentatively identified as methyl nitrophenols, although the specific isomers could not be identified. Both methyl nitrophenols were present at concentrations of about 45 ppb in the chamber. Thus these two compounds account for approximately 24 percent of the reacted o-cresol.

Phenol

Phenol was studied in the same manner as o-cresol, using 1 ppm (v/v) of phenol in the reacting mixture. Phenol suppressed the formation of O_3, PAN, formaldehyde, acetaldehyde, butanal, glyoxal, and methyl glyoxal, although not to the extent of the suppression observed for aniline or o-cresol. The disappearance rate of phenol was 0.113 hr-1, corrected for dilution. This rate implies a lifetime of about nine hours under photochemically active conditions.

Significant amounts of light scattering aerosol were produced in the phenol experiment. Maximum b_{scat} of 23 $x10^{-4}$ m^{-1} was observed after 90 minutes of reaction. After six hours of reaction, the chamber contents were sampled through a high purity quartz fiber filter. The mass collected corresponded to about nine percent of the reacted phenol in the aerosol phase. This is a lower limit to the actual aerosol phase distribution of phenol reaction products, since a substantial amount of the aerosol formed early in the experiment could have been lost to the chamber walls.

Three hours and 15 minutes into the phenol experiment a NaOH impinger sample was collected and analyzed for phenolic compounds. The major peak in the HPLC chromatogram was phenol itself. Agreement between the HPLC measurement of phenol and the direct gas chromatograph determination was within 12 percent. Two other peaks were observed in the HPLC chromatogram. These peaks have been identified as 4-nitrophenol and 2-nitrophenol. These are the same phenolic products reported for the nitrobenzene experiment. The estimated concentrations of these products are 10 ppb for 4-nitrophenol and 5 ppb for 2-nitro-phenol. Together, these two products account for approximately 11 percent of the reacted phenol.

METHODS DEVELOPMENT

Chromatographic Techniques

Laboratory Studies--

Phosgene--A considerable amount of effort was directed towards optimization of the phosgene determinative technique using the two standards generation systems described in the Experimental Section. Initial efforts were directed towards optimization of the aniline concentration. The

aniline concentration was varied from 0.2 to 2 percent using a 20 ppbv phosgene standard (produced by the dynamic dilution system previously described). The results of this experiment are shown in Table 9.

As shown in this table, good precision was achieved (for triplicate determination) at all three aniline concentrations, however the phosgene recovery declined steadily as the aniline concentration was decreased. Several experiments were conducted in which backup (series) impingers were placed in the sampling system and analyzed. No evidence of phosgene breakthrough was found in these experiments, even at the 0.2 percent aniline concentration.

In view of these data, a 2 percent aniline concentration was chosen for all further work. Several experiments were conducted to evaluate phosgene recovery as a function of concentration. Concentrations of 3 ppb or greater were generated using the dynamic dilution system, whereas lower concentrations were generated using the 17 cubic meter chamber in a static mode, as described in the Experimental Section. Recovery data for these experiments are shown in Table 10. Sampling volumes were 40 liters except for the 20 and 200 ppbv levels where only 10 liter samples were taken. Figure 15 shows a chromatogram for the 3 ppbv phosgene level. These data are very encouraging since quantitative recoveries were obtained at phosgene concentrations above 1 ppbv and precision (relative standard deviation) of 15 percent or better were obtained. Using redistilled aniline (described in the Experimental Section) blank levels of ~0.01 ppbv, based on a 40 liter sample volume were obtained. Without redistillation the blank levels were 0.03-0.05 ppbv.

Another laboratory evaluation of the phosgene method involved sampling humidified air, spiked with phosgene, using the dynamic dilution system previously described. Recoveries were tested at the 20 ppbv level using a 10 liter sampling volume. Data for this experiment are shown in Table 11. Although poor precision was observed at the 20 percent relative humidity point these results are very encouraging since quantitative recoveries were obtained over the entire range of humidities.

A final laboratory evaluation of the phosgene method involved comparison of the HPLC method, developed in this study, with a GC/ECD method reported in the literature[35]. This particular GC procedure appeared to be better

TABLE 9. EFFECT OF ANILINE CONCENTRATION ON PHOSGENE RECOVERY

Aniline Concentration Volume, %	Recovery, %	Standard Deviation
0.2	39	3
1.0	72	6
2.0	96	7

TABLE 10. PHOSGENE RECOVERY AS A FUNCTION OF CONCENTRATION

Phosgene Concentration, ppbv	Recovery, %	Standard Deviation
0.034	63	13
0.22	87	14
3.0	99	3
4.3	109	12
20	99	14
200	96	7

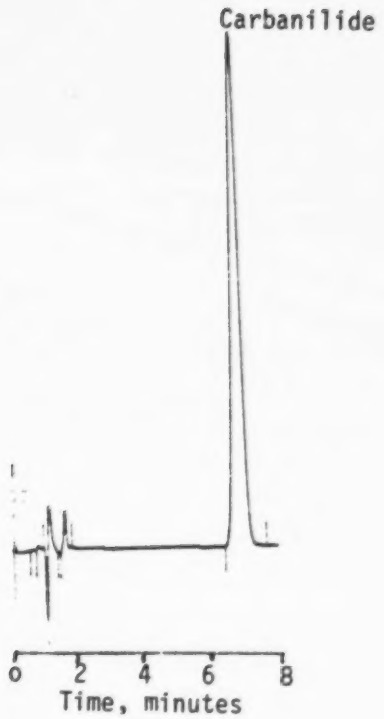

Figure 15. HPLC Chromatogram for 3 ppbv Phosgene Sample (see text for conditions).

TABLE 11. EFFECT OF HUMIDITY ON PHOSGENE RECOVERY

Relative Humidity, %	Recovery, %	Standard Deviation
5	92	19
20	106	40
60	100	1

than previously reported procedures, in that extensive preconditioning of the column using high concentrations of phosgene was not necessary. Although the GC procedure had apparently been tested only at 5 ppb concentrations and above, it was reported to give a detection limit of 0.1 ppbv. The method employs a 10 ft x 1/8 in OD Teflon column packed with Chromosil 310 operated at 45°C. In this study a one milliliter Teflon injection loop was used to introduce air directly from the chamber. The HPLC and GC/ECD procedures were compared by sampling from the 17 cubic meter chamber spiked with approximately 0.2 ppbv of phosgene, based on the measured rate of phosgene evolution from the permeation tube. Under these conditions values of 0.21 $\pm$0.07 and 0.12 $\pm$ 0.04 ppb were obtained for the GC/ECD and HPLC techniques, respectively. Unfortunately the GC/ECD technique cannot be readily calibrated at levels below approximately 3 ppbv because of the difficulty in generating accurate lower level standard. In contrast the HPLC technique can be easily calibrated using accurately prepared carbanilide solutions. In view of the uncertainty of the GC/ECD response at levels well below 3 ppbv, the comparison between the two techniques is relatively good. However, more work should be conducted using low level gas phase phosgene standards to prove the reliability of these techniques at typical ambient concentrations (0.01-0.05 ppbv).

Formyl Chloride--As mentioned in the Experimental Section, formyl chloride is too unstable at room temperature to prepare a test atmosphere of known concentration. Therefore experiments were conducted using formanilide, the expected derivatization product of formyl chloride, spiked into the sample impinger. Recoveries of 89 $\pm$ 12 and 74 $\pm$ 13 were achieved for spike levels of 0.1 and 12 micrograms, respectively. These levels represent 0.3 and 36 ppbv of formyl chloride in a 60 liter sample. A typical chromatogram is shown in Figure 16. Additional data for formyl chloride in ambient air are presented in a subsequent portion of this report.

Acyl Chlorides--Several attempts were made to generate stable atmospheric concentrations of mono-, di-, and tri-chloroacetyl chlorides in both the 200 liter and 17 cubic meter chambers. However, in all cases the compounds were shown to disappear, presumably through chemical reaction, within a

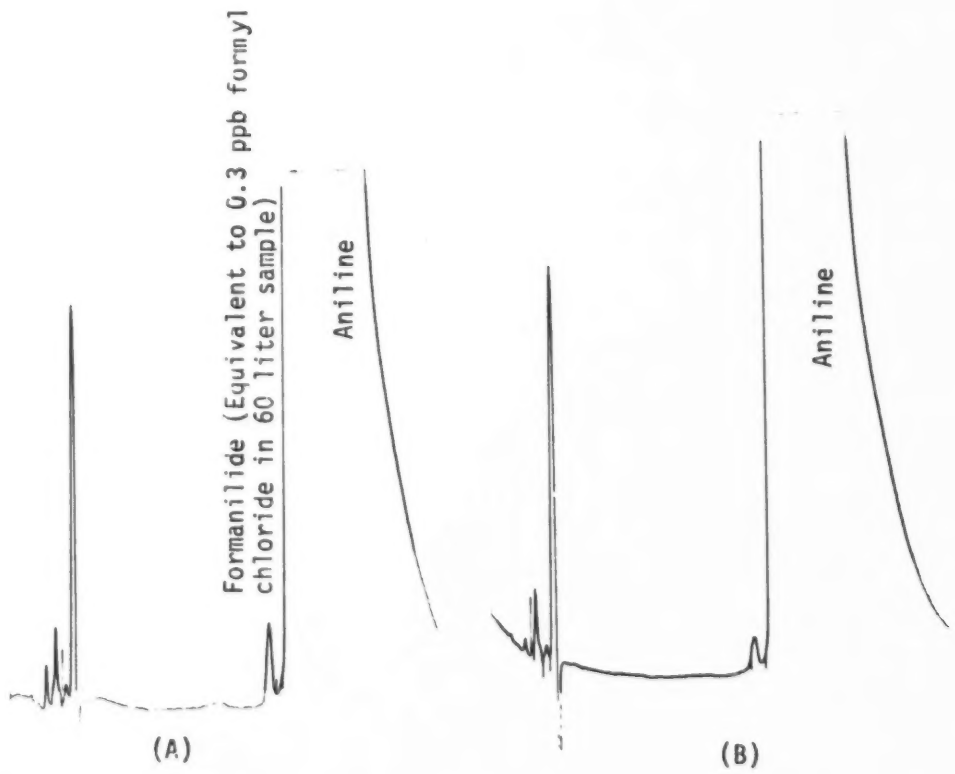

Figure 16. Chromatograms for Impinger Samples. (A) Spiked with 100 ng of Formanilide and (B) Unspiked. (see text for conditions)

matter of a few hours. Consequently the sampling and analysis method was tested by introducing low level hexane solutions of the compounds at various points in the procedure. The results for these experiments are summarized in Table 12. For experiments involving the collection of sample after spiking, a 20 liter volume of high purity air (Aadco clean air generator) was drawn through the impinger at a rate of 1 liter per minute. Figure 17 shows a chromatogram for the 1 ug spike level.

Based on these data the procedure appears to be viable although the recovery for trichloroacetyl chloride is rather poor at the lowest test concentration (corresponding to 0.22 ppbv for a 60 liter sample).

Field Studies--

The methods described previously for phosgene, formyl chloride and chloroacetylchlorides were evaluated by collecting a variety of ambient air samples at the Arthur Kill electrical generating station on Staten Island. These samples were collected on May 1, 1983. Samples were split and analyzed for the various compounds of interest. The data obtained are presented in Table 13. These results must be regarded as preliminary since no existing techniques are sufficiently sensitive to confirm the identities of the compounds being detected. Representative chromatograms for the various analyses are shown in Figures 18 and 19.

The data presented in Table 13 indicate phosgene levels of 0.07 to 0.19 ppbv, after blank correction (at the time of these analyses the distillation procedure for aniline purification had not been established and therefore blank levels in the 0.05 ppbv range were obtained). Furthermore the phosgene level did increase slightly at midday compared to the morning samples, as expected based on its presumed formation via photochemical degradation of chlorinated hydrocarbon pollutants. In order to reduce the phosgene blank level further, a series of samples was collected using 0.2 percent, rather than 2 percent, aniline in toluene. Previous data in Table 10 showed that at this aniline concentration a phosgene recovery of approximately 40 percent was obtained. As shown in Table 13, Sample 11 did drop to approximately 40 percent of the Sample 10 value as expected, whereas the blank level dropped by a factor of five. Similar data were obtained for the Sample 5/7 pair. Although not conclusive, these data tend to verify the authenticity of the phosgene data since

TABLE 12. RECOVERY DATA FOR CHLOROACETYLCHLORIDES

Description of Experiment	% Recovery ± Standard Deviation		
	Chloroacetyl-chloride	Dichloro-Acetylchloride	Trichloro-Acetylchloride
Chloroacetanilides (1 ug each) spiked into impinger prior to sample workup.	150 ± 10	102 ± 8	104 ± 10
Chloroacetylchlorides (1 ug each) spiked into impinger.	74 ± 7	73 ± 2	95 ± 4
Chloroacetylchlorides (1 ug each) spiked into inlet arm of impinger prior to sampling.	82 ± 3	85 ± 13	90 ± 7
Same as above except only 0.1 ug spike level.	81 ± 13	78 ± 7	53 ± 18

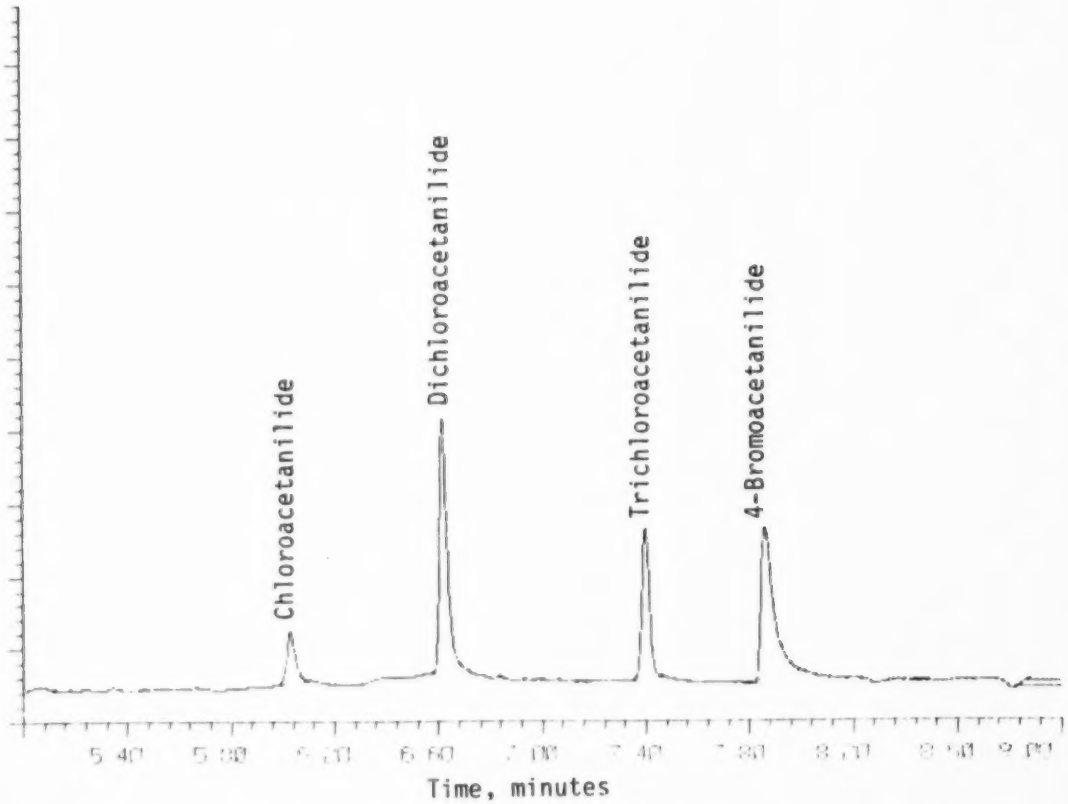

Figure 17. GC/ECD Chromatogram for Acylchlorides Spiked Into the Impinger Inlet Arm at the 1 µg Level Before Sampling (see text for conditions).

TABLE 13. EXPERIMENTAL RESULTS FROM STATEN ISLAND FIELD SAMPLES, 5/1/83

Sample #	Time	T(°C)	%RH	Aniline Conc.(%)	Sample Volume (Liters)	Concentration (ppbv)*				
						Phosgene	Formyl Chloride	CAC	DCAC	TCAC
1	0900	68	70	2	60	0.08	NA	0.10	0.02	0.02
2	0945	68	70	2	60	0.07	0.64	NA	NA	NA
3	1016	69	70	2	60	0.07	NA	NA	NA	NA
4	(Backup for #3)			2	60	0.04	NA	NA	NA	NA
5	1049	69	70	2	100	0.09	NA	<0.05	<0.02	<0.02
6	(Backup for #5)			2	100	0.03	NA	<0.05	<0.02	<0.02
7	1142	70	70	0.2	100	0.04	<0.07	NA	NA	NA
8	(Backup for #7)			0.2	100	0.02	<0.07	NA	NA	NA
9	1233	72	70	2	60	0.19	0.09	NA	NA	NA
10	1304	74	70	2	100	0.14	0.27	NA	NA	NA
11	1404	76	65	0.2	60	0.05	NA	<0.05	<0.02	<0.02
Blank	--	--	--	2	--	0.05**	0.14**	NA	NA	NA
Blank	--	--	--	0.2	--	0.01**	NA	<0.05	<0.02	<0.02

* Blank corrected.

** 100 liter volume assumed.

NA = Not analyzed.

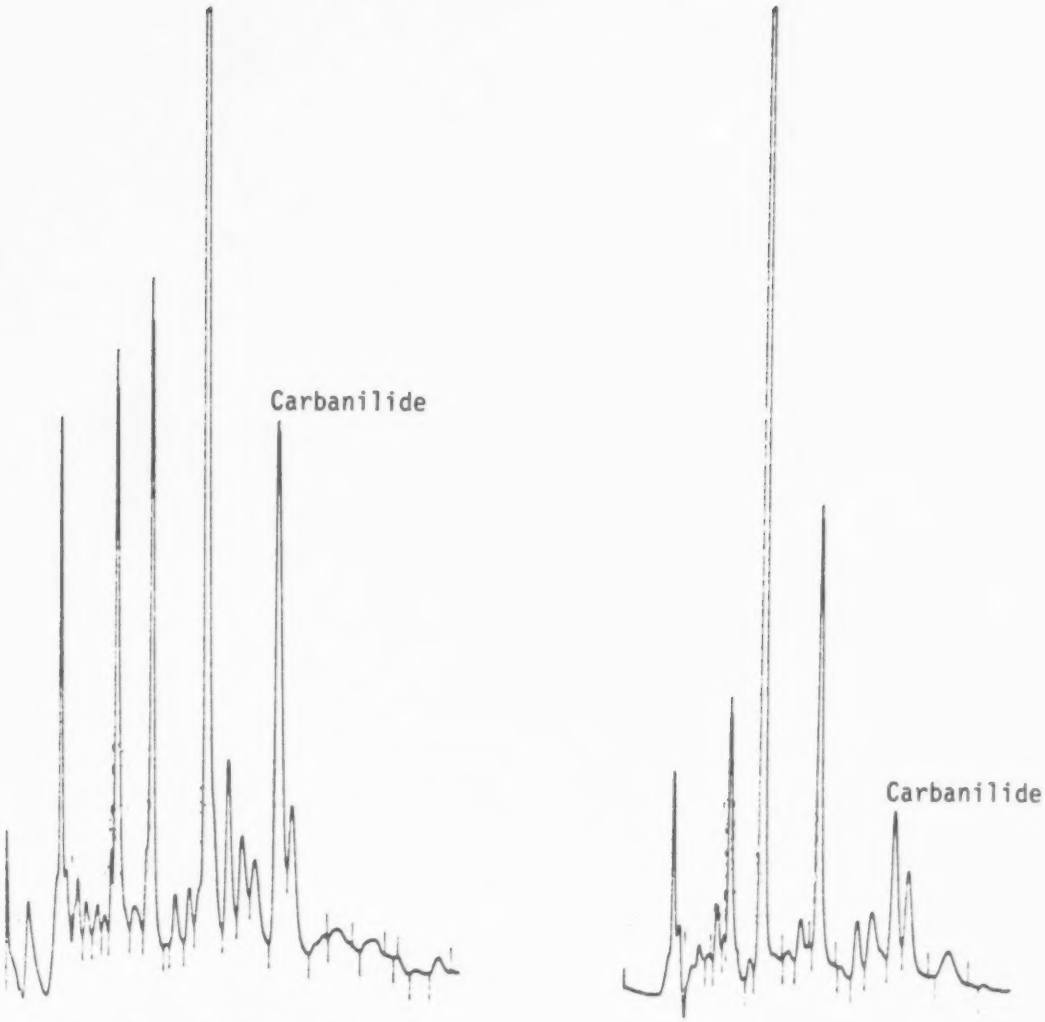

Figure 18. HPLC Chromatograms for Phosgene Analyses of Staten Island Samples (see text for conditions).

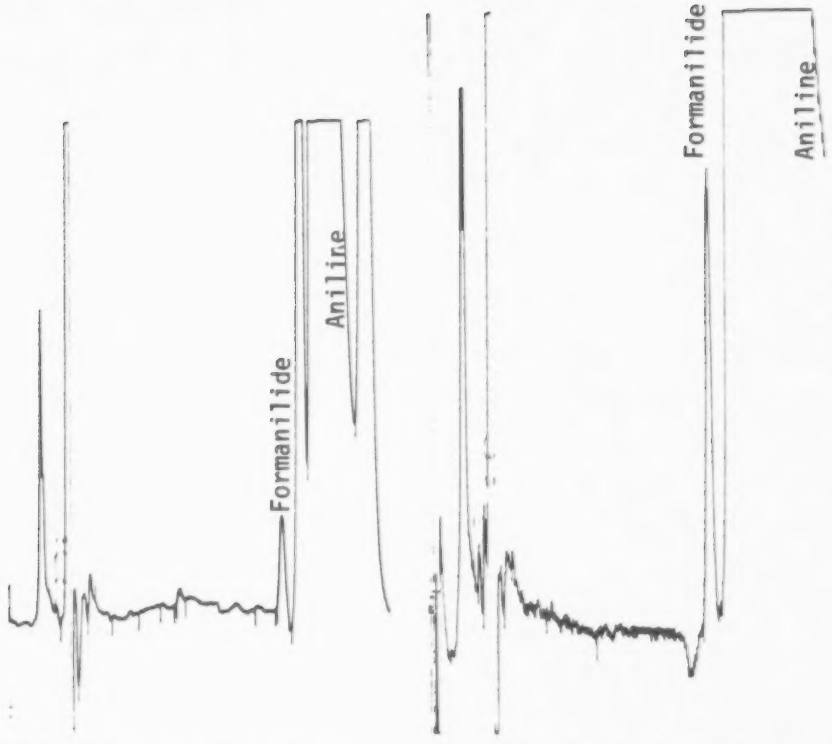

Figure 19. HPLC Chromatograms of Formyl Chloride Analyses from Staten Island Samples (see text for conditions).

artifactual formation of carbanilide would be expected to decrease more dramatically with the 10 fold decrease in aniline concentration. Nonetheless, more extensive evaluation of the phosgene method is required to verify its usefulness in determining ambient concentrations of phosgene.

Scattered results were obtained for formyl chloride in that its presence, above the blank level, was indicated in only three of the five samples. Furthermore, no consistent pattern in the observed formyl chloride levels was obvious. The relatively high blank level of 0.14 ppbv was a contributing factor in the variability of the data, since the highest formyl chloride concentration observed was only four times greater than the blank level. Much more work is needed to verify the presence of formyl chloride in ambient air at the levels indicated.

Only a single sample indicated any acylchlorides to be present. The first sample collected appeared to contain a small amount (0.1 ppbv) of the monochloro compound. This single positive value is not sufficient to establish the presence of chlorinated acylchlorides in ambient air. In fact, the absence of any of the three acylchlorides in the midday samples casts doubt on the authenticity of the single positive value observed, since both phosgene and the acylchlorides are presumed to be formed from photochemical degradation of chlorinated hydrocarbons.

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